

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08F 8/00, C08J 5/18 // (C08F 210/02, 220:06)</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/11929</b> <b>(43) International Publication Date:</b> 4 May 1995 (04.05.95)
<b>(21) International Application Number:</b> PCT/US94/12366 <b>(22) International Filing Date:</b> 27 October 1994 (27.10.94) <b>(30) Priority Data:</b> 08/143,799 27 October 1993 (27.10.93) US 08/144,173 27 October 1993 (27.10.93) US <b>(71) Applicant:</b> CHEVRON CHEMICAL COMPANY [US/US]; P.O. Box 5047, San Ramon, CA 94583-0947 (US). <b>(72) Inventors:</b> WANG, James, H.; 1325 E. Overland Road, Appleton, WI 54915 (US). ROSENDALE, David; 205 Len Drive, Mauriceville, TX 77632 (US). KURKOV, Victor, P.; 66 Dunfries Terrace, San Rafael, CA 94901 (US). THEARD, Leslie, P.; 10050 Westpark #1003, Houston, TX 77042 (US). CHING, Ta, Yen; 10 Santa Yorma Court, Novato, CA 94945 (US). COMPTON, Lewis, R.; 2705 East Tanager Trails, Orange, TX 77632 (US). EICHELBERGER, Mitchell, P.; 42 Meadowridge Place, Woodlands, TX 77381 (US). PALMGREN, Tor, H., G.; 2509 International Avenue, Orange, TX 77632 (US). <b>(74) Agents:</b> HOLLAND, Charles, D. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).	<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(54) Title:</b> LOW-HAZE IONOMERS OF COPOLYMERS OF ALPHA-OLEFINS, CARBOXYLIC ACID ESTERS, AND OPTIONAL COMONOMERS, AND PROCESSES FOR MAKING AND ACIDIFYING THESE IONOMERS		
<b>(57) Abstract</b>  Ionomer compositions which have improved optical properties are disclosed. These compositions comprise ionomers which can be represented as the polymerization product of alpha-olefins having from two to eight carbon atoms, esters of alpha, beta-ethylenically-unsaturated carboxylic acids, metal salts of acrylic and methacrylic acid, and optional alpha, beta-ethylenically-unsaturated comonomers which impart some desired polymer property or properties, such as acidity and/or solvent resistivity. Also disclosed are methods of making these ionomer compositions in a reactive extruder and treating the compositions with acid to impart acidity to the compositions or to only the surface of the compositions.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

1     LOW-HAZE IONOMERS OF COPOLYMERS OF ALPHA-OLEFINS, CARBOXYLIC  
2         ACID ESTERS, AND OPTIONAL COMONOMERS, AND PROCESSES FOR  
3         MAKING AND ACIDIFYING THESE IONOMERS

4                     BACKGROUND

5     This invention provides new polymeric ionomer compositions  
6     which have low haze. Low haze makes the compositions  
7     especially suited for use in clear packaging films, in  
8     addition to the other applications in which ionomers are  
9     utilized. This invention also provides a method for making  
10    these new polymeric compositions and for modifying the  
11    acidity of the compositions.

12    The compositions comprise ionomers which can be represented  
13    as the polymerization product of alpha-olefins having from  
14    two to eight carbon atoms, esters of alpha, beta-  
15    ethylenically-unsaturated carboxylic acids, metal salts of  
16    acrylic and methacrylic acid, and optional alpha, beta-  
17    ethylenically-unsaturated comonomers which impart some  
18    desired polymer property or properties, such as acidity  
19    and/or solvent resistivity. These ionomer compositions can  
20    easily be formed into films.

21    Ionomers which can be formed into films and methods of  
22    making ionomers are known in the art. Although these  
23    previously-known ionomers have similar chemical constituents  
24    to the ionomer compositions of this invention, the known  
25    ionomers have significantly different properties from the  
26    compositions of this invention. In addition, the known  
27    processes for making ionomers are also quite different from  
28    the method of making compositions of the present invention.

29    Japanese patent number Sho 49-31556 to Iwami et al., dated  
30    Aug. 22, 1974, discloses a process for making ionomers which  
31    comprises saponifying copolymers of ethylene and alpha,

- 2 -

1     beta-ethylenically-unsaturated carboxylate esters with a  
2     basic metal compound in aliphatic alcohol or in an organic  
3     solvent containing an aliphatic alcohol. The copolymer is  
4     homogeneously or heterogeneously dispersed in the alcohol  
5     solution. The saponified product can be further acidified  
6     to provide a composition having acid groups. Although the  
7     ionomers which have acid functionality are said to have low  
8     haze, no haze values are provided for ionomers which have no  
9     acid functionality.

10    Japanese patent number Sho 53-134591 to Harada et al., dated  
11    Nov. 24, 1978, discloses a film made by the process of Sho  
12    49-31556 which is said to be useful for stretch-wrap  
13    applications. Their ionomer comprises a copolymer having  
14    90-98 mole percent ethylene, 9.7 to 2.0 mole percent of an  
15    alkyl ester of an unsaturated carboxylic acid, 0 to 2.5 mole  
16    percent of unsaturated carboxylic acid, and 0.3 to 2.5 mole  
17    percent of a metal salt of an unsaturated carboxylic acid.  
18    It is stated that their film has very good mechanical,  
19    thermal, and optical properties, but the film is limited to  
20    having less than 9.7 mole percent ester because blocking  
21    occurs between film layers. In addition, the copolymer is  
22    limited to a maximum of 2.5 mole percent metal salt of an  
23    unsaturated carboxylic acid due to the viscosity of the  
24    copolymer being too high to allow processing of the  
25    copolymer. All copolymers in the films of the examples  
26    contain an unsaturated carboxylic acid component, which, the  
27    patent states, are used to adjust the modulus of elasticity  
28    and transparency of the film.

29    U.S. patent number 5,218,057, issued to V. Kurkov and  
30    L. Theard on June 8, 1993 and which is incorporated by  
31    reference in its entirety, teaches a process for saponifying  
32    an ethylene alkyl acrylate copolymer which comprises adding  
33    an aqueous solution of an inorganic alkali metal base to a

- 3 -

1 molten ethylene-alkyl acrylate copolymer and mixing the  
2 alkali metal base and copolymer at a temperature sufficient  
3 for saponification to take place and at which the ethylene-  
4 alkyl acrylate copolymer remains in a molten or fluid state.  
5 Copolymers made by this process have lower tensile strength,  
6 lower gloss, and much higher haze than the copolymers of the  
7 present invention.

8 U.S. patent number 4,638,034 to McClain, dated Jan. 20, 1987  
9 and which is incorporated by reference in its entirety,  
10 claims a process for preparing an ethylene-acrylic acid  
11 copolymer salt which comprises saponifying an ethylene-alkyl  
12 acrylate copolymer in the molten state, in the absence of  
13 solvent or water other than by-product alkanol, with alkali  
14 metal hydroxide or alkaline earth metal hydroxide under non-  
15 static mixing conditions so as to thereby form alkanol and  
16 an alkali metal or alkaline earth metal salt of ethylene-  
17 acrylic acid copolymer, and separately recovering the  
18 alkanol and the salt.

19 U.S. patent number 3,970,626 to Hurst et al., dated July 20,  
20 1976, discloses a copolymer of ethylene, alkyl acrylate or  
21 methacrylate, and an alkali metal salt of acrylic or  
22 methacrylic acid. Although this patent is mainly concerned  
23 with forming copolymers which form stable aqueous emulsions,  
24 the patent states that the copolymer can be extruded into  
25 films of good flexibility. Copolymers in the examples are  
26 formed using a batch autoclave. It is stated that about a  
27 one-fold excess of sodium hydroxide over what is  
28 theoretically required is used to convert the ester groups.

29 U.S. patent number 4,042,766 to Tatsukami et al., dated Aug.  
30 16, 1977 and which is incorporated by reference in its  
31 entirety, provides a method for preparing ionically cross-  
32 linked copolymers comprising melt-blending a copolymer

- 4 -

1 comprising 1) ethylene and 2) at least one alkyl acrylate or  
2 methacrylate where the alkyl is selected from the group  
3 consisting of isopropyl or tert-butyl, with 3) at least one  
4 metal compound selected from the group consisting of  
5 acetates, formates, and oxides of zinc, magnesium, calcium,  
6 and sodium, and maintaining the molten blend at a  
7 temperature of about 200 to 320°C. The patent states that  
8 high mixing efficiency is desirable in the reaction  
9 equipment to assure uniform dispersion of the metal compound  
10 into the ester copolymer and to assure quick evaporation of  
11 the low molecular-weight byproducts, such as by melt-  
12 blending the components. Per the patent, adequate mixing  
13 was provided by a 20 mm-diameter single-screw extruder  
14 having a retention time of about one minute, as illustrated  
15 in Example 1 of that patent.

16 U.S. patent number 3,789,035 to Iwami et al., dated Jan. 29,  
17 1974 and which is incorporated by reference in its entirety,  
18 discusses three methods for acidifying an ionomer of a  
19 copolymer of ethylene and an ester of an alpha, beta-  
20 ethylenically-unsaturated carboxylic acid. The ionomer is  
21 made by saponifying a copolymer of ethylene and an ester of  
22 an alpha, beta-ethylenically-unsaturated carboxylic acid  
23 with a basic metal compound in a solvent containing an  
24 alcohol. The patent states that the alcohol is used to  
25 promote the reaction of the basic metal compound with the  
26 copolymer. The ionomer is then acidified by either 1)  
27 adding acid and replacing some of the basic metal with  
28 hydrogen; 2) melt-blending a polymer having acid groups with  
29 an ionomer; or 3) exchanging a non-alkali metal ion with the  
30 alkali metal ion on the ionomer which has been dispersed in  
31 a solvent.

32 U.S. patent number 3,264,272 to Rees, dated Aug. 2, 1966,  
33 claims a composition comprising a random copolymer of an

- 5 -

1     alpha-olefin having from two to ten carbon atoms, an alpha,  
2     beta-ethylenically-unsaturated carboxylic acid having from  
3     three to eight carbon atoms in which 10 to 90 percent of the  
4     acid is neutralized with metal ions, and an optional third  
5     mono-ethylenically unsaturated comonomer such as methyl  
6     methacrylate or ethyl acrylate. This copolymer is acidic  
7     due to the carboxylic acid groups present in the copolymer.  
8     U.S. patent number 3,404,134 discloses the process for  
9     making these compositions, which comprises reacting an  
10    ethylene acrylic acid copolymer with a metal compound at a  
11    pressure between 100 and 10,000 psi and a temperature above  
12    the melt-point of the copolymer.

13    U.S. patent number 5,189,113 to Muehlenbernd et al., dated  
14    Feb. 23, 1993, discloses a process for making ionically  
15    cross-linked copolymers of ethylene and alpha, beta-  
16    ethylenically-unsaturated carboxylic acids or alpha, beta-  
17    ethylenically-unsaturated comonomers donating carboxyl  
18    groups, such as anhydrides. This process requires reacting  
19    the copolymer with a solid metal compound in a mixing zone  
20    of a twin-screw extruder and subsequently pumping in water.  
21    The advantages for this process are said to be that no  
22    discoloration of the ionomer occurs because no corrosion of  
23    the twin-screw extruder occurs, and no specks of unreacted  
24    solid metal compound are found in the ionomer film.

25    U.S. patent number 5,003,001 to Hasenbein et al., dated Mar.  
26    26, 1991, claims a process for making ionically cross-linked  
27    copolymers of ethylene and alpha, beta-ethylenically-  
28    unsaturated carboxylic acids or alpha, beta-ethylenically-  
29    unsaturated comonomers donating carboxyl groups, such as  
30    anhydrides. This process reacts the copolymer with an  
31    aqueous metal salt solution in a first reaction zone at a  
32    temperature from 140 to 180°C to form ionomer and completely  
33    devolatilizes the ionomer in a second, three-stage

- 6 -

1 devolatilization zone at a temperature from 200 to 270°C.  
2 This process is said to provide odor-free ionomer film which  
3 is free of specks.

4 Although there has been much research in the area of  
5 ionomers, what has been lacking in the prior art is  
6 optically clear ionomers comprising copolymers of alpha  
7 olefins having two to eight carbon atoms, esters of alpha,  
8 beta-ethylenically-unsaturated carboxylic acids, and metal  
9 salts of alpha, beta-ethylenically-unsaturated carboxylic  
10 acids as well as methods of making those ionomers. This  
11 invention provides such compositions and methods.

12 SUMMARY OF THE INVENTION

13 In one embodiment, the invention comprises a copolymer of  
14 alpha-olefins having from two to eight carbon atoms, esters  
15 of alpha, beta-ethylenically-unsaturated carboxylic acids  
16 having from four to twenty-two carbon atoms, and metal salts  
17 of acrylic or methacrylic acid, wherein this copolymer has a  
18 haze of no more than ten percent as measured by ASTM method  
19 D 1003.

20 In one preferred embodiment, the invention comprises a  
21 copolymer of ethylene, methyl acrylate, and sodium salt of  
22 acrylic acid, wherein the haze of the copolymer is no more  
23 than five percent.

24 In another embodiment, the invention comprises a method of  
25 making an ionomer composition. This method comprises  
26 contacting a Group IA metal-containing solution with a  
27 molten or fluid copolymer comprising alpha-olefins having  
28 from two to eight carbon atoms and esters of alpha, beta-  
29 ethylenically-unsaturated carboxylic acids having from four  
30 to twenty two carbon atoms and having a melt index between  
31 about 100 and about 2000 g/10 min., as measured by ASTM



- 7 -

1 method D 1239 at 190°C using a 2.16 kg weight; and  
2 intensively mixing the copolymer and Group IA metal-  
3 containing solution at a temperature and to an extent which  
4 provides an ionomer composition having no more than ten  
5 percent haze.

6 In another embodiment, the invention comprises a method of  
7 reducing the water solubility of an ionomer composition  
8 formed into a shape such as strands, pellets, or film, which  
9 method comprises contacting a surface of the shape with an  
10 acid.

11 Among other factors, the present invention is based on our  
12 finding that films of the composition as described herein  
13 have very low haze, particularly when the films are made  
14 after saponifying a copolymer as described above under  
15 conditions which include intensive mixing, a greater extent  
16 of saponification, and higher reaction temperatures. Film  
17 haze is no more than ten percent, and many films have a haze  
18 of no more than five or even two percent. Furthermore, in a  
19 preferred embodiment, the composition has improved  
20 properties such as improved tensile strength, hot tack  
21 strength, and/or heat seal strength over ionomers of similar  
22 composition.

23 In addition to the properties discussed above, many of the  
24 compositions of this invention have no acidity, regardless  
25 of the extent of saponification. These advantages and  
26 others are further described below.

27 DESCRIPTION OF THE FIGURES

28 Figure 1 is a scanning electron micrograph of a freeze-  
29 fractured cross-section of 3-mil thick film made from an  
30 ionomer composition of this invention, taken at a  
31 magnification factor of 8,000.

- 8 -

1 Figure 2 is a scanning electron micrograph of a freeze-  
2 fractured cross-section of 3-mil thick film of ionomer of  
3 Comparative Example G. Figure 2 illustrates that spherical  
4 and oblong ionic clusters or regions are present in the  
5 ionomer. This micrograph was also produced at a  
6 magnification factor of 8,000.

7 A JEOL JSM-820 scanning electron microscope was used to  
8 generate the micrographs. The micrographs of Figures 1 and  
9 2 show the fracture surface of films which were made by the  
10 blown film process of the examples.

11 Figure 3 shows the hot-tack of ionomer of this invention  
12 from Example 24 as a function of temperature. The ordinate  
13 is temperature in °C, and the abscissa is hot-tack, measured  
14 in Newtons/inch. Line 1 is 35% hydrolyzed ionomer, line 2  
15 is 42% hydrolyzed ionomer, and line 3 is 50% hydrolyzed  
16 ionomer.

17 Figure 4 shows the heat seal strength of the  
18 ionomer/polyethylene film of Example 26 as a function of  
19 temperature. The ordinate is temperature in °F and the  
20 abscissa is the heat seal strength in lb/inch.

## 21 DETAILED DESCRIPTION OF THE INVENTION

### 22 A) Compositions

23 Compositions of this invention can be represented as the  
24 copolymerization product which contains the following  
25 comonomers:

- 26 (a) alpha-olefins having from 2 to 8 carbon atoms,
- 27 (b) esters of alpha,beta-ethylenically-unsaturated  
28 carboxylic acids,

- 9 -

- 1 (c) metal salts of acrylic or methacrylic acid, and  
2 (d) optionally, other alpha, beta-ethylenically-unsaturated  
3 comonomers which impart desirable polymer properties.

4 These compositions have no more than ten percent haze,  
5 preferably no more than seven percent haze, and more  
6 preferably, no more than five percent haze. The most  
7 preferred compositions have no more than two percent haze.  
8 Additionally, these compositions have very good hot tack  
9 strength, heat seal strength, and mechanical properties such  
10 as tensile strength. Acid functionality can also be  
11 introduced into these ionomers.

12 Examples of compositions of this invention include ethylene-  
13 methyl acrylate-sodium acrylate ionomer, ethylene-methyl  
14 methacrylate-sodium methacrylate ionomer, ethylene-ethyl  
15 acrylate-sodium acrylate ionomer, ethylene-propylene-methyl  
16 acrylate-sodium acrylate ionomer, ethylene-propylene-methyl  
17 methacrylate-sodium methacrylate ionomer, ethylene-methyl  
18 acrylate-lithium acrylate ionomer, ethylene-methyl acrylate-  
19 potassium acrylate ionomer, ethylene-methyl acrylate-  
20 cobalt(II) or (III) acrylate ionomer, ethylene-methyl  
21 acrylate-zinc acrylate ionomer, ethylene-methyl acrylate-  
22 titanium(II), (III), or (IV) acrylate ionomer, ethylene-  
23 methyl acrylate-magnesium acrylate ionomer, ethylene-methyl  
24 acrylate-iron(II) or (III) acrylate ionomer, ethylene-methyl  
25 acrylate-nickel(II) or (III) acrylate ionomer, ethylene-  
26 methyl acrylate-copper(I) or (II) acrylate ionomer,  
27 ethylene-methyl acrylate-acrylic acid-sodium acrylate  
28 ionomer, ethylene-methyl methacrylate-methacrylic acid-  
29 sodium methacrylate ionomer, ethylene-methyl acrylate-sodium  
30 acrylate ionomer grafted with maleic anhydride, ethylene-  
31 methyl acrylate-maleic anhydride-sodium acrylate ionomer,

- 10 -

1 and acrylic acid-grafted-(ethylene-methyl acrylate-sodium  
2 acrylate) ionomer.

3 Monomer (a) comprises alpha-olefins having from 2 to 8  
4 carbon atoms. Preferably, monomer (a) comprises alpha-  
5 olefins having from 2 to 3 carbon atoms, and more  
6 preferably, monomer (a) consists essentially of ethylene.

7 Monomer (b) comprises esters of alpha, beta-ethylenically-  
8 unsaturated carboxylic acids having from 4 to 22 carbon  
9 atoms. Preferably, monomer (b) has from 4 to 13 carbon  
10 atoms, and more preferably has from 4 to 8 carbon atoms.  
11 Examples of monomer (b) include methyl acrylate, methyl  
12 methacrylate, ethyl acrylate, ethyl methacrylate, butyl  
13 acrylate, and butyl methacrylate. Methyl acrylate is the  
14 preferred monomer (b).

15 Monomer (c) is a metal salt of acrylic or methacrylic acid.  
16 The metal ion is selected from Group IA, Group IIA, and  
17 transition metal ions. The metal ions may also be aluminum,  
18 gallium, germanium, and tin. Other examples include  
19 lithium, sodium, potassium, rubidium, cesium, calcium,  
20 magnesium, zinc, titanium, iron, cobalt, nickel, and copper.  
21 Preferably, the metal ion is a Group IA or Group IIA metal  
22 ion, and more preferably, the metal ion is a Group IA metal  
23 ion. Most preferred is sodium. Monomer (c) is about 25 to  
24 99 mole percent of the total amount of (b) and (c) present  
25 in a composition. Preferably, monomer (c) is about 35 to  
26 80, and more preferably, is about 40 to 60, mole percent of  
27 the total amount of (b) and (c) present in a composition.

28 Typically, a composition of this invention contains from  
29 about 1 to 20 mole percent of monomers (b) and (c) in total.  
30 Preferably, a composition contains about 3.5 to 12.5 mole  
31 percent, and more preferably, about 5.5 to 10 mole percent

- 11 -

1 of monomers (b) and (c). Most preferred is a composition  
2 containing about 7.5 to 10 mole percent of monomers (b) and  
3 (c).

4 Monomer (d) is an alpha, beta-ethylenically-unsaturated  
5 comonomer which imparts certain desired polymer properties.  
6 The amount and type of monomer (d) is determined by the  
7 particular properties that are desired in the final  
8 composition. For example, monomer (d) may be acrylic or  
9 methacrylic acid which is present in an amount that provides  
10 the desired acid functionality to the composition. Other  
11 examples of monomer (d) include maleic anhydride and maleic  
12 acids to impart acidity, acrylonitrile to impart solvent  
13 resistance, and styrene to increase the rigidity of the  
14 composition. Typically, the compositions contain 0 to 10  
15 mole percent of monomer (d). Preferred compositions contain  
16 0 to 5 mole percent of monomer (d).

17 Monomer (d) can also be added by grafting a group such as  
18 acrylic acid or maleic anhydride to a composition of the  
19 present invention or to one of the composition's precursors.  
20 As a result, compositions can comprise grafted (ethylene,  
21 (meth)acrylate, metal salt of (meth)acrylic acid)  
22 copolymers. Maleic anhydride-grafted (ethylene, methyl  
23 acrylate, sodium acrylate) copolymer is one such  
24 composition.

25 The ionomer compositions of this invention have a number of  
26 surprising features which distinguish them from other  
27 ionomers having similar chemical constituents. The ionomers  
28 of this invention are quite clear. Haze is typically no  
29 more than 5 percent. Also, in one preferred embodiment, the  
30 60° gloss is typically at least 100, and in many instances,  
31 is at least 120. In another preferred embodiment, tensile  
32 strength of the composition is improved over ionomers of

- 12 -

1 similar composition by 100-300 percent. Hot-tack strength  
2 and heat seal strength can also be improved over ionomers of  
3 similar composition. Combinations of these improved  
4 features are present in some preferred compositions of this  
5 invention.

6 For example, the haze, gloss, and tensile strength of  
7 ionomer of this invention are substantially different from  
8 the haze, gloss, and tensile strength of ionomer made by the  
9 process of U.S. Pat. № 5,218,057. Ethylene-methyl acrylate  
10 copolymer having about 20 weight percent (about 7.5 mole  
11 percent) methyl acrylate and having about 65% of the methyl  
12 acrylate saponified with aqueous sodium hydroxide according  
13 to the process of U.S. Pat. № 5,218,057 had a haze of 15%  
14 and 60° gloss of 66. Tensile strength of an ethylene-methyl  
15 acrylate copolymer having 20 weight percent methyl acrylate  
16 which had about 60% of the methyl acrylate groups saponified  
17 with aqueous sodium hydroxide according to the process of  
18 U.S. Pat. № 5,218,057 was 1582 psi in the machine direction.  
19 A composition of the present invention made by saponifying  
20 an ethylene-methyl acrylate copolymer having about 20 weight  
21 percent methyl acrylate with aqueous sodium hydroxide to  
22 convert about 65% of the methyl acrylate groups had a haze  
23 of 2%, gloss of 133, and tensile strength in the machine  
24 direction of 4010 psi.

25 The ionomers of this invention also can be formed into very  
26 thin film. When blowing film, the blow-up ratio can be as  
27 high as 2:1 to about 2.5:1. Typically, a film of ionomer of  
28 this invention can have a thickness of less than about 1  
29 mil. Film having a thickness of about 0.5 mil has been  
30 made, and film having a thickness of about 0.2 - 0.3 mil can  
31 be made on conventional processing equipment.

- 13 -

1 The morphology of prior art ionomers can also differ  
2 substantially from the morphology of ionomers of this  
3 invention. The morphology of prior art ionomers can also  
4 differ substantially from the morphology of ionomers of this  
5 invention. Prior-art ionomers can contain highly localized  
6 and large clusters of ionic material dispersed throughout  
7 the ionomer. Scanning-electron micrographs have shown that  
8 these clusters can range in size from about 0.05 micron to  
9 greater than 1 micron in size.

10 Figure 2 is a scanning-electron micrograph for the ionomer  
11 of Comparative Example G. This ionomer consists essentially  
12 of ethylene, 5.7 mole percent methyl acrylate, and 1.8 mole  
13 percent of the sodium salt of acrylic acid. The spherical  
14 or oblong ionic clusters evident in this micrograph range in  
15 size from about 0.1 micron to about 0.5 micron. The  
16 clusters were determined to be ionic by energy-dispersive  
17 X-ray spectroscopy, which showed a higher sodium content  
18 within the clusters when compared to the surrounding  
19 continuous phase.

20 Figure 1 is a scanning-electron micrograph for ionomer  
21 composition of this invention, which consists essentially of  
22 ethylene, 3.7 mole percent methyl acrylate, and 3.7 mole  
23 percent of the sodium salt of acrylic acid. This ionomer  
24 composition is substantially free of ionic clusters of the  
25 size seen in Figure 2, since essentially no ionic clusters  
26 are observed in this micrograph. An ionomer composition  
27 which is substantially free of ionic clusters contains  
28 essentially no ionic clusters about 0.05 micron in size or  
29 larger when a freeze-fractured cross-section of 3-mil thick  
30 blown film which is made by the method of Example 1 is  
31 viewed with a scanning electron microscope at a  
32 magnification factor of 8,000. An ionomer composition which  
33 is substantially free of ionic clusters will also have a

- 14 -

1 haze of no more than ten percent. The ionomer composition  
2 of Figure 1 corresponds to the composition of Example 12,  
3 which had a haze of 3%. The large flecks of debris in  
4 Figure 1 are believed to be foreign matter. The flecks are  
5 not regions having high sodium content.

6 Additives well-known in the art may be included in the  
7 ionomer, such as anti-block and slip additives and anti-  
8 oxidants. Preferably, the composition of this invention  
9 also contains a polymeric acid having a molecular weight of  
10 less than about 10,000, such as ethylene acrylic acid.  
11 Ionomer compositions containing these low molecular weight  
12 acids are disclosed in copending U.S. Ser. No. 08/188,848,  
13 filed Jan. 31, 1994, which is incorporated by reference in  
14 its entirety herein.

15 B) Method for making the compositions

16 One method for making compositions of this invention  
17 comprises saponifying a copolymer having ester groups with a  
18 Group IA metal-containing solution. To obtain the clear  
19 ionomer compositions of this invention, it is important to  
20 provide intensive mixing of the copolymer and the Group IA  
21 metal-containing solution and to have a temperature and/or  
22 extent of saponification high enough that a substantially  
23 uniform saponification of the copolymer occurs. This method  
24 minimizes the production of localized ionomer regions or  
25 domains, which appear as the spherical and oblong ionic  
26 clusters of Figure 2. This method also permits a greater  
27 extent of saponification of the copolymer without obtaining  
28 a saponified product that has so high of a viscosity that it  
29 cannot be formed into a film on conventional equipment.

30 Intensive mixing of the reaction components results from  
31 selection of reactants with the appropriate physical and  
32 chemical characteristics and selection of the proper



- 15 -

1 processing conditions. Particular processing conditions are  
2 discussed below for a reactive extruder. However, the  
3 general principles disclosed therein apply to processes  
4 which are equivalent to saponifying a copolymer with a  
5 Group IA metal-containing solution in a reactive extruder.

6 (1) Reactants

7 (a) Copolymer to be saponified

8 The copolymers which are saponified comprise copolymers of  
9 ethylene, esters of alpha, beta-ethylenically-unsaturated  
10 carboxylic acids, and optional alpha, beta-ethylenically-  
11 unsaturated comonomers which impart desirable polymer  
12 properties. Typically, these copolymers contain from about  
13 1 to 20 mole percent of esters of alpha, beta-ethylenically-  
14 unsaturated carboxylic acids in total. Preferably, the  
15 copolymers contain about 2 to 20 mole percent, more  
16 preferably 3.5 to 12.5 mole percent, and even more  
17 preferably, about 5.5 to 12.5 mole percent of esters of  
18 alpha, beta-ethylenically-unsaturated carboxylic acids in  
19 total. Most preferred are those copolymers containing about  
20 6.5 to 10 mole percent of esters of alpha, beta-  
21 ethylenically-unsaturated carboxylic acids. The preferred  
22 esters are alkyl acrylates. Preferably, the alkyl group  
23 contains from one to eight carbon atoms, and more preferably  
24 contains from one to four carbon atoms. Methyl is a  
25 preferred alkyl group.

26 Examples of the copolymers which are saponified include  
27 ethylene-methyl acrylate copolymer, ethylene-methyl  
28 methacrylate copolymer, ethylene-ethyl acrylate copolymer,  
29 ethylene-propylene-methyl acrylate copolymer, ethylene-  
30 propylene-methyl methacrylate copolymer, ethylene-methyl  
31 acrylate-acrylic acid copolymer, ethylene-methyl  
32 methacrylate-methacrylic acid copolymer, maleic anhydride-  
33 grafted-ethylene-methyl acrylate copolymer, ethylene-methyl

- 16 -

1 acrylate-maleic anhydride copolymer, acrylic acid-grafted-  
2 ethylene-methyl acrylate copolymer, and ethylene-methyl  
3 acrylate-butyl acrylate copolymer. Preferably, the  
4 copolymers are ethylene-methyl acrylate copolymer, ethylene-  
5 methyl methacrylate copolymer, ethylene-ethyl acrylate  
6 copolymer, maleic anhydride-grafted-ethylene-methyl acrylate  
7 copolymer, and ethylene-methyl acrylate-butyl acrylate  
8 copolymer. Most preferred is ethylene-methyl acrylate  
9 copolymer.

10 The melt index of copolymers to be saponified should be  
11 between about 100 and 2000, preferably between about 200 and  
12 800, and more preferably between about 300 and 600 grams/10  
13 minutes. Copolymers having higher melt-index values are  
14 preferred when it is desired to have a saponified  
15 composition with a higher melt index. One process for  
16 making these copolymers comprises polymerizing ethylene,  
17 alkyl acrylate and/or alkyl methacrylate, and the optional  
18 comonomer in autoclaves using free-radical initiation  
19 catalysts. This process is described in U.S. Patent  
20 № 3,350,372, which is incorporated by reference in its  
21 entirety. The copolymers of the examples were made by this  
22 method, unless specified otherwise. In one preferred  
23 embodiment, the ethylene-alkyl acrylate copolymer is made by  
24 the process described in copending U.S. Ser. No. 07/947,870,  
25 filed Sep. 21, 1992 (published as WO 93/06137), which is  
26 incorporated by reference in its entirety herein. Copolymer  
27 made by this process has a substantially higher melt-point  
28 temperature than the copolymer made by the process of U.S.  
29 Patent No. 3,350,372. The ionomer of this invention has  
30 high melt point temperature and high clarity when made with  
31 this copolymer. Another process for producing copolymers  
32 useful in making the ionomer compositions of this invention  
33 comprises free-radical polymerization of ethylene and alkyl  
34 acrylate and/or alkyl methacrylate as described above,

- 17 -

1 followed by reactive extrusion with a compound such as  
2 acrylic acid or maleic anhydride. Alternatively, grafting  
3 may be performed after saponification. A particularly  
4 preferred copolymer is ethylene-methyl acrylate copolymer  
5 having between about 5.5 and 12.5 mole percent methyl  
6 acrylate and having a melt index of about 400 g/10 min.,  
7 available from Chevron Chemical Company as EMAC® copolymer.

8 (b) Group IA metal-containing solution

9 The Group IA metal-containing solution comprises a Group IA  
10 metal in a solvent, which solvent does not prevent  
11 saponification of an ester by the Group IA metal. The  
12 solvent is preferably one which evaporates readily under  
13 devolatilization conditions typically encountered in  
14 reactive extruders. Solvents can be organic or inorganic,  
15 and common solvents include water, alcohols, and  
16 polyethylene glycols, with water being preferred.

17 The Group IA metal-containing solution has at least one  
18 Group IA metal present. Preferably, the solution comprises  
19 an aqueous solution of a Group IA metal oxide and/or  
20 hydroxide, such as oxides and hydroxides of lithium, sodium,  
21 potassium, rubidium, and/or cesium. Preferably, the  
22 Group IA metal-containing solution comprises aqueous sodium  
23 hydroxide or aqueous potassium hydroxide.

24 It is important that the overall concentration of metals in  
25 the Group IA metal-containing solution is low enough that  
26 the solution is capable of being mixed uniformly and  
27 intensively with melted copolymer in a reaction section of a  
28 reactive extruder. However, it is preferred to have only  
29 that amount of solvent present that is necessary to provide  
30 this capability. Normally, a sufficient quantity of solvent  
31 is present when the Group IA metal-containing solution  
32 contains little or no excess solvent beyond that required to

- 18 -

1 solubilize essentially all of the Group IA metal and other  
2 metals present. Thus, for example, 50% aqueous caustic  
3 solution is preferred over 35% aqueous caustic solution.

4 The Group IA metal-containing solution may optionally  
5 contain other metal oxides, hydroxides, and/or salts which  
6 supply cations for monomer (c). The metal ions can be  
7 alkaline earth or transition-element metals. Specific  
8 examples of these metals include calcium, magnesium, zinc,  
9 titanium, cobalt, nickel, and copper. Typical anions  
10 include hydroxide, halide, acetate, propionate, decanoate,  
11 and stearate ions, with acetate ions being preferred anions.  
12 The hydroxide form is also preferred.

13 Instead of being present in the Group IA metal-containing  
14 solution, metal ions (including Group IA metal ions) may  
15 optionally be incorporated into the ionomer composition of  
16 this invention by other methods. One method is to first  
17 saponify a copolymer by the method of this invention, then  
18 totally or partially replace the ion of this ionomer  
19 composition with other metal ions under ion-exchange  
20 conditions, or to react the ionomer composition with an  
21 aqueous metal hydroxide. For example, an ion-exchange  
22 solution comprising an aqueous solution of zinc oxide or  
23 zinc acetate may be mixed with a sodium ionomer composition  
24 of this invention in a section of a reactive extruder to  
25 replace at least a portion of the sodium ions with zinc  
26 ions.

27 Examples of metal ions which may be exchanged include the  
28 alkaline metals, alkaline earth metals such as magnesium,  
29 transition metals such as titanium, cobalt, copper, and  
30 zinc, and other metal ions such as aluminum, gallium,  
31 germanium, and tin.

- 19 -

1     The anion of a salt used to ion-exchange the ionomer is  
2     preferably one which is easily washed out of the ionomer and  
3     separated from it during filtration. Alternatively, the  
4     anion is preferably one which forms an easily-evolved  
5     compound or one which evolves or whose products of  
6     decomposition evolve at devolatilization conditions in a  
7     reactive extruder. Typical anions include chloride,  
8     acetate, propionate, decanoate, and stearate ions. Acetate  
9     ions are preferred.

10             (2) Reactive Extruder

11     A reactive extruder which is useful in producing  
12     compositions of this invention comprises an extruder having  
13     a copolymer feed section, one or more reaction sections, a  
14     subsequent devolatilization section, and an extrusion  
15     section. Typically, these sections are separately jacketed  
16     to allow for heating or cooling within each section. These  
17     sections can also be vented with one or more vent ports per  
18     section to allow the escape of volatile components, such as  
19     the solvent for the Group IA metal solution and byproducts  
20     of the saponification reaction, such as alcohols.  
21     Generally, the reactive extruder will also have optional  
22     means for introducing reactants into any reaction sections  
23     as well as means for mixing components in the reaction  
24     section(s) and means for conveying the components through  
25     the extruder. Typically, the means for mixing and conveying  
26     components to be reacted are screws.

27     Reactive extruders can have a single screw or multiple  
28     screws. Each screw typically has a central shaft with a  
29     key-way or spline upon which mixing elements are secured.  
30     The reactive extruder may have either co-rotating or  
31     counter-rotating screws.

- 20 -

1 Typically, copolymer to be reacted is fed to the screw  
2 through a loss-in-weight feeder, and the solid copolymer is  
3 melted in a feed section of the reactive extruder. In some  
4 embodiments, all reactants (i.e. copolymer and Group IA  
5 metal-containing solution) can be fed to the reactive  
6 extruder through a feed section. In a preferred embodiment,  
7 copolymer is introduced into the reactive extruder in a feed  
8 section, and the Group IA metal-containing solution is fed  
9 to one or more reaction sections. A devolatilization  
10 section is a convenient means for removing any solvent and  
11 byproducts of the saponification reaction from the  
12 saponified composition. Equivalent or additional means for  
13 removing volatile components can be used, however, such as  
14 drying the ionomer composition under reduced pressure in a  
15 falling-film evaporator.

16 One reactive extruder which was particularly effective in  
17 producing compositions of this invention is a Werner-  
18 Pfleiderer co-rotating and intermeshing twin-screw extruder.  
19 The reactive extruder had a feed section, a reaction  
20 section, a devolatilization section, and a pressurization or  
21 pumping section which pushed the product through an  
22 extrusion die. The devolatilization section had a first  
23 portion which was vented to a condenser maintained at  
24 atmospheric pressure, and a second portion of the  
25 devolatilization section was vented with sufficient vacuum  
26 and capacity to remove essentially all of the volatile  
27 components from compositions prior to conveying and  
28 extruding them.

29 Typically, copolymer pellets are introduced into a feed  
30 section of a reactive extruder, where the pellets are heated  
31 and worked by the screw to form molten or fluid copolymer.  
32 The screw elements also convey the molten copolymer from  
33 this feed section to a first reaction section, where the

- 21 -

1 molten copolymer and Group IA metal-containing solution are  
2 mixed intensively.

3 Intensive mixing can be supplied by incorporating one or  
4 more reverse-flow elements along with neutral or reverse-  
5 flow kneading blocks on the screw in a reaction zone. The  
6 copolymer to be saponified and the Group IA metal-containing  
7 solution should be mixed as uniformly and as quickly as  
8 possible to provide a fairly uniform reaction of metal-  
9 containing solution with the molten copolymer. Mixing  
10 should be of sufficient intensity that saponification of  
11 only localized areas is prevented.

12 This intensive mixing is of greater intensity than that  
13 required in the prior-art processes of U.S. Pat. № 4,638,034  
14 and U.S. Pat. № 4,042,766. For example, a Werner-Pfleiderer  
15 Model ZSK-40 twin-screw reactive extruder had the  
16 configuration of screw elements detailed in Table 1 column  
17 A. This screw design provided intensive mixing of the  
18 Group IA metal-containing solution with copolymer in the  
19 reaction section through a combination of left-handed  
20 elements and neutral kneading blocks. It is believed that  
21 the left-handed elements in the reaction section provide  
22 momentary retardation of polymer flow in addition to a shear  
23 zone due to impeded and/or reversed flow of the reaction  
24 mass, while the neutral kneading blocks imparted intensive  
25 mixing and promoted additional shear. Most of the  
26 compositions of this invention were produced at a screw  
27 speed of about 400 to 550 rpm. High screw speeds help to  
28 assure intensive mixing.

TABLE 1

ELEMENT NUMBER	COLUMN A	COLUMN B	COLUMN C

- 22 -

1	1	40/20 <sup>1</sup>	PKR/10 <sup>2</sup>	PKR/10
2	2	60/60	20/10	20/10
3	3	60/60	42/42	42/42
4	4	40/40	42/42	42/42
5	5	40/40	42/42	28/28
6	6	40/40	28/28	28/28
7	7	40/20	28/28	28/28
8	8	40/40	20/20	20/20
9	9	25/25	20/20	20/20
10	10	KB45/5/40 <sup>3</sup>	20/20	20/20
11	11	KB45/5/40	KB45/5/28	20/10
12	12	25/25	KB45/5/28	KB45/5/28
13	13	25/25	20/20	KB45/5/28
14	14	25/25	20/20	20/20
15	15	40/20 LH <sup>4</sup>	KB90/5/28	20/20
16	16	25/25	20/10 LH	20/10 LH
17	17	KB90/5/40	20/20	20/10 LH
18	18	25/25	20/20	20/10 LH
19	19	KB90/5/40	KB45/5/28	20/20
20	20	25/25	20/10	20/20
21	21	40/20 LH	20/20	KB45/5/28
22	22	25/25	20/20	20/10
23	23	KB90/5/40	KB90/5/28	20/20
24	24	25/25	20/20	20/20
25	25	KB90/5/40	KB45/5/14 LH	KB90/5/28
26	26	25/25	KB45/5/14 LH	20/20
27	27	40/20 LH	20/20	KB45/5/14 LH
28	28	KB45/5/20 LH	20/20	KB45/5/14 LH
29	29	25/25	KB90/5/28	20/20
30	30	25/25	20/20	20/20
31	31	25/25	20/20	KB90/5/28
32	32	25/25	20/20	20/20
33	33	25/25	20/20	20/20
34	34	40/40	20/20	20/20

SUBSTITUTE SHEET (RULE 26)



- 23 -

1	35	40/40	KB90/5/28	20/20
2	36	40/40	20/20	KB90/5/28
3	37	KB45/5/20 LH	20/20	20/20
4	38	40/40	20/20	20/20
5	39	40/40	20/20	20/20
6	40	40/40	20/20	20/20
7	41	40/40	20/20	KB90/5/28
8	42	25/25	20/20	20/20
9	43	25/25	20/20	20/20
10	44	25/25	KB90/5/28	20/10
11	45	25/25	20/20	20/20
12	46	25/25	20/20	20/20
13	47	25/25	20/10 LH	20/20
14	48	25/25	20/10 LH	20/20
15	49	25/25	20/20	20/20
16	50	25/25	20/20	20/20
17	51	25/25	20/20	20/20
18	52	25/25	20/20	20/20
19	53	25/25	42/42	20/20
20	54	25/25	42/42	20/20
21	55	25/25	42/42	42/42
22	56		20/20	42/42
23	57		20/20	42/42
24	58		20/20	28/28
25	59		20/20	20/20
26	60		20/20	20/20
27	61			20/20

## 28 NOTES:

- 29 1. All elements were right-handed elements unless  
30 designated otherwise. The first number is the pitch,  
31 given in distance (mm) traveled in one revolution. The  
32 second number is the length of the element (mm).

- 24 -

- 1        2.    The PKR element is a wedge-shaped adapter which  
2           provides a taper from the 1/2 inch shaft to the first  
3           element of the screw.  
4        3.    KB indicates a kneading block. The first number is the  
5           angle formed by the paddles on the kneading block when  
6           compared to the line through the screw shaft, in  
7           degrees. The second number is how many paddles are on  
8           one element. The third number is the length of the  
9           element (mm).  
10      4.    "LH" indicates a left-handed element.

11                    (3) Reaction conditions

12    Reaction temperature, feed-rate of reactants, and extent of  
13    saponification are also important processing parameters when  
14    making compositions of this invention.

15                    (a) Reaction temperature

16    Compositions of this invention are typically produced where  
17    the barrel temperature in the reaction section(s) of the  
18    extruder is between about 200 and 350°C, although some clear  
19    ionomers were prepared at a temperature between about 150  
20    and 200°C. Any reaction temperatures discussed herein refer  
21    to the barrel temperatures of the extruder. The actual  
22    temperature of the melted polymer is believed to be lower  
23    than the measured barrel temperature because of heat-  
24    transfer limitations.

25    Preferably, the reaction temperature is between 225 and  
26    350°C, and, more preferably, the temperature is between  
27    about 275 and 350°C. The upper limit of the temperature  
28    range is determined by the temperature at which the  
29    copolymer or composition degrades. The lower limit of the  
30    temperature range is the temperature at which 1) the  
31    copolymer to be reacted is in a molten or fluid state;  
32    2) essentially all of the Group IA metal in the Group IA

- 25 -

1 metal-containing solution is consumed by the saponification  
2 reaction within the reaction section; and 3) the composition  
3 being extruded remains visually clear. As a general rule,  
4 higher reaction temperatures as specified in the more  
5 preferable range above provide low-haze ionomers more  
6 consistently than lower reaction temperatures.

7 (b) Feed rate of reactants

8 The Group IA metal-containing solution is fed in an amount  
9 that is effective to achieve the desired extent of  
10 saponification of the copolymer being fed to the reactive  
11 extruder. Typically, essentially all of the Group IA metal  
12 in solution reacts with the copolymer. The Group IA metal-  
13 containing solution may be fed to a reaction section batch-  
14 wise or continuously, or it may be fed intermittently so  
15 that the solution is mixed intimately and rapidly with the  
16 molten copolymer. A continuous feed is preferred. The  
17 Group IA metal-containing solution may also be split between  
18 multiple reaction sections and be fed continuously and/or  
19 intermittently to any reaction section.

20 The copolymer to be saponified is fed to the reactive  
21 extruder at a rate high enough that the molten polymer forms  
22 a molten polymer seal between consecutive segments of a  
23 reaction section and between a reaction section and a  
24 devolatilization section. This seal can be formed by having  
25 a reverse-flow screw element at the desired seal location.  
26 The feed-rate should also be low enough that the reaction  
27 mass comprising the copolymer to be saponified and the  
28 Group IA metal-containing solution does not move through the  
29 reaction section so quickly that the reaction mass is not  
30 mixed intensively. The feed-rate should also be low enough  
31 that the extruded polymer is visually clear, corresponding  
32 to no more than ten percent haze.

- 26 -

1 The copolymer to be saponified may be fed to the extruder  
2 batch-wise, intermittently or continuously. A continuous  
3 feed is preferred to provide a commercially-attractive  
4 process which is easily and effectively controlled.

5 Typically, the average residence time for reactants in a  
6 Werner & Pfleiderer ZSK-40 twin-screw extruder which has a  
7 feed section, one reaction section, devolatilization  
8 section, and pumping section is about 30 to about 40 seconds  
9 at a continuous feed-rate of approximately 100 lb./hr. of  
10 polymer to be saponified and at a screw speed of about 500  
11 rpm. The average residence time in the reaction section of  
12 this reactive extruder at these conditions is typically  
13 about 5 to about 15 seconds.

14 When the feed-rate is too high to make a composition of this  
15 invention, the screw torque will decrease, and the ionomer  
16 will turn cloudy. Both of these conditions can be observed  
17 almost immediately upon feeding too much copolymer to the  
18 extruder. Visually, the extruded copolymer turns from clear  
19 to cloudy, and when a strand of the cooled copolymer is  
20 pulled in the direction in which it was extruded, the cloudy  
21 copolymer turns whitish and opaque.

22 (c) % saponified

23 The extent of saponification is defined as the percent of  
24 moles of esters of alpha, beta-ethylenically-unsaturated  
25 carboxylic acids converted to metal salts of acrylic and  
26 methacrylic acid. Compositions of this invention have been  
27 produced where the extent of saponification of the ester  
28 groups in the copolymer has been between about 25 and 99%.  
29 Ionomer which has an extent of saponification below about  
30 25% above are typically cloudy and have poorer gloss, melt  
31 strength, and/or tensile strength than compositions of this  
32 invention. A greater extent of saponification generally

- 27 -

1 produces low-haze ionomers more consistently than a low  
2 extent of saponification, particularly when the reaction  
3 temperature is between about 150 and 225°C.

4 C) Acidification

5 Acidification of a polymer is a useful method for modifying  
6 polymer properties. In one preferred embodiment, ionomers  
7 of this invention have essentially no acidity. These  
8 ionomers can be represented as copolymers comprising  
9 comonomers of alpha-olefins, esters of alpha, beta-  
10 ethylenically-unsaturated carboxylic acids, and metal salts  
11 of alpha, beta-ethylenically-unsaturated carboxylic acids.  
12 The properties of these non-acidic ionomers can be modified  
13 by adding acid groups.

14 Also, some of the ionomers of this invention are highly  
15 water-dispersible. This can be an advantage for  
16 applications where repulpable compositions are desired, such  
17 as repulpable paper coatings and adhesives. However, water  
18 dispersibility is a problem where the ionomer composition is  
19 cooled in a water-bath after saponification, which is a  
20 common commercial method of cooling polymers. Much of the  
21 ionomer to be cooled can end up dispersed in the cooling  
22 water, turning the water a milky white color.

23 Other cooling means may be used for handling highly water-  
24 dispersible ionomers, such as hot-face cutting or utilizing  
25 an air-cooled conveyor or a conveyor which has a water-  
26 chilled surface to cool the polymer strands or pellets.  
27 However, these methods are more expensive and less efficient  
28 than passing hot polymer in the form of strands, pellets, or  
29 film through a water bath, and these methods require the  
30 installation of new equipment in many existing commercial  
31 ionomer production facilities. In addition, ionomer may  
32 discolor when using these cooling means, since the ionomer

- 28 -

1 rapidly oxidizes when it is maintained at elevated  
2 temperatures for the extended periods of time inherent in  
3 these other cooling means.

4 (1) Cooling ionomer in an aqueous acid bath

5 In a preferred embodiment, highly water-dispersible ionomer  
6 of this invention may be cooled in an acid bath to prevent  
7 dispersion of much of the ionomer. Highly water-dispersible  
8 ionomer typically has a high sodium acrylate content which  
9 makes the ionomer water-soluble. It is believed that ion  
10 exchange occurs predominantly on the surface of the polymer  
11 when passing hot ionomer strands through the acid bath,  
12 replacing metal ions on the surface of the polymer with  
13 hydrogen ions from the acid. It is believed that this makes  
14 the surface of the strands or pellets acidic and  
15 substantially reduces their water solubility.

16 Infrared analysis of ionomer pellets which were cooled in an  
17 acid bath detected no acid groups. However, it is believed  
18 that the concentration of acid groups in the overall ionomer  
19 pellets was so small that it was undetectable by infrared  
20 analysis of the bulk ionomer.

21 Almost any inorganic or water-soluble organic acid can be  
22 used in the acid bath. A dilute aqueous solution of a non-  
23 oxidizing acid is preferred to reduce processing cost and to  
24 improve the washing efficiency when rinsing any excess acid  
25 off of the polymer. The following list is illustrative of  
26 the types of acids which may be used: sulfuric acid, formic  
27 acid, propionic acid, oxalic acid, and the like. Preferred  
28 acids are hydrochloric acid, phosphoric acid, and acetic  
29 acid.

30 The temperature of the acid solution is preferably that  
31 temperature which produces ionomer which has not discolored

- 29 -

1 and which provides ionomer at the appropriate temperature  
2 for any subsequent processing steps, such as drying. The  
3 temperature of the acid solution is typically between about  
4 5 to 50°C, and preferably is between about 10 and 30°C.

5 Example 16 illustrates this method for cooling ionomer using  
6 an aqueous acid solution.

7 (2) Acidification of a clear copolymer of  
8 ethylene and esters and metal salts of alpha,  
9 beta-ethylenically-unsaturated carboxylic  
10 acids

11 In one embodiment, compositions of this invention have  
12 carboxylic acid groups, in which case the compositions can  
13 be represented as copolymers comprising comonomers of alpha-  
14 olefins, esters of alpha, beta-ethylenically-unsaturated  
15 carboxylic acids, metal salts of alpha, beta-ethylenically-  
16 unsaturated carboxylic acids, and alpha, beta-ethylenically-  
17 unsaturated carboxylic acids. Acid groups can plasticize  
18 the composition and increase its melt index. This permits  
19 tailoring of polymer properties such as polymer flow  
20 viscosity, tear strength, polymer reactivity with food, and  
21 odor or taste for a particular application.

22 Acidification of a composition comprising a copolymer of  
23 alpha-olefins, esters of alpha, beta-ethylenically-  
24 unsaturated carboxylic acids, and metal salts of alpha,  
25 beta-ethylenically-unsaturated carboxylic acids can occur in  
26 a reaction section of a reactive extruder. Preferably,  
27 acidification occurs in a second reaction section when using  
28 reactive extrusion, and preferably after the composition  
29 comprising the reaction product of a copolymer of alpha-  
30 olefins and esters of alpha, beta-ethylenically-unsaturated  
31 carboxylic acids has been saponified with a Group IA metal-  
32 containing solution in a first reaction section.

- 30 -

1 Other equipment may be used in place of a reactive extruder  
2 for acidification of a saponified composition. For example,  
3 a Brabender Plasticorder, a resin kettle, or an autoclave  
4 may be used.

5 A non-oxidizing acid can be used at a temperature and in a  
6 concentration which does not cause significant degradation  
7 of the copolymer or composition. Typically, the amount of  
8 acid required is the amount which provides the desired  
9 weight percent of acid groups per combined weight of acid  
10 and copolymer to be acidified. Examples of these acids  
11 include phosphoric acid, hydrochloric acid, benzoic acid,  
12 lactic acid, and stearic acid. Polymeric non-oxidizing  
13 acids can also be used, such as ethylene-acrylic acid  
14 copolymer, exemplified by Dow Chemical Company's Primacor  
15 Grade 3330. The non-oxidizing acids may have only one or  
16 two monomer units, such as benzoic acid or acetic acid, or  
17 they may comprise polymeric acids having multiple monomer  
18 units and having a molecular weight well in excess of one  
19 million, such as Primacor Grade 3330. Phosphoric acid,  
20 lactic acid, and polymer acids are preferred. Typical  
21 temperatures for acidification are between about 190 and  
22 300°C, and preferably are between about 230 and 300°C. The  
23 acid concentration is preferably between 10 and 95%.

24 In certain applications or compositions of this invention,  
25 any byproducts of acidification can remain in the  
26 composition. For other applications or compositions, any  
27 byproducts of acidification and/or any excess acid can be  
28 removed from the ionomer by washing with water or other  
29 solvent and filtering the composition. For example, polymer  
30 acidified using phosphoric acid can be washed with water in  
31 an autoclave. The byproduct salt in the aqueous phase can  
32 subsequently be separated from the polymer by filtration.



- 31 -

1                   (3) Acidification of hazy non-acidic ionomer to  
2                   improve clarity

3       Acid can also be used to improve the clarity of an ionomer  
4       which has high haze and little or no acid functionality  
5       present before acidification. This provides an easy and  
6       inexpensive means for rendering these opaque polymers less  
7       hazy or even clear. In a preferred embodiment, the adhesion  
8       of the acidified polymer improves as well. In another  
9       preferred embodiment, the melt index of the ionomer also  
10      increases.

11     The ionomer to be acidified has a haze greater than 10% but  
12     otherwise has the same chemical analysis of components as  
13     described in the preceding section for adding acid functions  
14     to a clear but non-acidic ionomer composition of this  
15     invention. Acidification is also preferably performed as  
16     described in the preceding section. Uniform mixing of the  
17     acid and ionomer, as supplied by a reactive extruder, for  
18     example, provides a consistent and clearer acidified  
19     ionomer. In the examples, the haze of the ionomer to be  
20     acidified exceeded 90% and could be reduced in half and even  
21     by 75%.

22     The previous section also specifies the types of acids  
23     useful for acidifying hazy ionomers. The amount of acid  
24     required for acidification is that amount which provides an  
25     ionomer film having at most half of the haze that was  
26     present in the non-acidified ionomer. The amount of acid  
27     used also should not exceed that amount which is necessary  
28     to provide the greatest reduction in haze for the particular  
29     ionomer and acid used. As Tables 22 and 23 show, haze  
30     begins to increase again once the amount of acid is  
31     increased beyond the amount necessary to provide minimum  
32     haze for the particular ionomer and acid. Therefore, excess

- 32 -

1 acid beyond the amount required to reduce the haze to its  
2 minimum value is to be avoided.

3 When the acidified ionomer is analyzed, as little as 0.05  
4 mole of acidic monomer need be present in the ionomer per  
5 mole of the saponified monomer that was originally present  
6 in the ionomer prior to acidification. For example, when  
7 ethylene-methyl acrylate-sodium acrylate ionomer having  
8 greater than 10% haze is made from ethylene-methyl acrylate  
9 copolymer having 20 weight percent methyl acrylate which is  
10 25% hydrolyzed using aqueous sodium hydroxide, the ionomer  
11 has approximately 5.4 weight percent sodium acrylate, or  
12 about 1.9 mole percent sodium acrylate. Acidification of at  
13 least 5% of the sodium acrylate groups decreases the haze of  
14 this ionomer. Preferably, the amount of acidic monomer in  
15 the acidified ionomer is greater than 0.07 mole per mole of  
16 hydrolyzed monomer present in the non-acidified ionomer, and  
17 preferably the amount of acidified ionomer is greater than  
18 0.1 mole per mole. Examples 20-23 illustrate this method of  
19 making clearer ionomers from hazy ionomers.

20 D) Uses of the compositions

21 Ionomer compositions of this invention can be formed into  
22 single or multi-layer films using conventional equipment.  
23 For example, cast, extruded, or blown film can be made.

24 An ionomer composition of this invention can be coextruded  
25 with or laminated to other polymers such as nylon  
26 (unoriented and oriented), polyester (unoriented and  
27 oriented), polystyrene, vinyl acetate, polyacrylonitrile,  
28 polyvinylidene dichloride, and polyolefins such as  
29 polypropylene (unoriented and oriented), polyethylene (low  
30 density, high density, and linear low density), ethylene-  
31 methyl (meth)acrylate copolymers, ethylene-ethyl  
32 (meth)acrylate copolymers, ethylene-(meth)acrylic acid  
33 copolymers, ethylene-vinyl alcohol copolymers, ethylene

- 33 -

1 vinyl acetate copolymers, and other polymers and their  
2 derivatives capable of being coextruded. Typical uses for  
3 ionomer compositions of this invention include their use in  
4 single-layer or multi-layer films, where they can be used as  
5 tie layers or used for imparting flexibility, strength, hot  
6 tack, and/or heat seal capabilities. Such uses include  
7 stretch films, bundling (shrink) wrap, food and drug  
8 packaging, and skin packaging for protecting the contents of  
9 a package.

10 Single-layer ionomer film or multi-layer film in which the  
11 ionomer is on one face of the film can be used as a surface  
12 protection layer for products such as glass, polycarbonate  
13 or poly(methyl methacrylate) products, which can be used in  
14 windshields for vehicles or windows. The ionomer layer  
15 protects products from scratches and/or nicks because of the  
16 ionomer's abrasion resistance. The ionomer's adhesion to  
17 such substrates is excellent, yet it can be peeled readily  
18 from the surface. The transparency of the ionomer of this  
19 invention allows visual inspection of the surface of the  
20 wrapped product, permitting a customer to inspect a product  
21 for flaws prior to receipt and unwrapping of the product.

22 Single-layer ionomer film or multi-layer film containing  
23 ionomer of this invention can be used to make easy-open  
24 packaging such as easy-tear film, bags, pouches and parcels.  
25 A tear propagates linearly through the film, and the  
26 Elmendorf tear strength of the ionomer indicates that it is  
27 well-suited to uses such as easy-opening packaging. The  
28 package in which the film is incorporated normally is  
29 notched or incorporates a tear strip to facilitate ease of  
30 opening of the package.

31 The ionomer of this invention can also serve as its own tie  
32 layer due to its good adhesion to other layers. This

- 34 -

1 eliminates the need for separate tie layers in a multi-layer  
2 film, reducing the thickness of the multi-layer film and  
3 reducing the overall cost of making the multi-layer film.

4 Ionomer compositions of this invention may also be used in  
5 thermally extruded and thermally formed products such as  
6 automotive interior parts and skin packaging. The ionomer  
7 compositions may be used alone or in combination with other  
8 polymers in blow-molded or injection molded articles,  
9 particular where such articles need to be grease- and oil-  
10 resistant such as bottles for fragrances or detergents, and  
11 the compositions may also be used in articles such as food  
12 trays formed by vacuum thermo-forming. The ionomer  
13 compositions of this invention may be used in making  
14 articles such as golf ball covers; coated fabrics;  
15 orthopedic, prosthetic and medical devices; recreational  
16 equipment; and footwear components. The ionomer  
17 compositions of this invention are especially useful in  
18 applications where the ionomer properties discussed above,  
19 as well as the excellent abrasion resistance, transparency,  
20 and/or directional tear properties of the ionomer, are  
21 useful.

22 Theories discussed herein are intended to provide possible  
23 explanations for what was observed. These theories are not  
24 to be interpreted as limiting the invention described  
25 herein. Also, the following examples are illustrative and  
26 are not intended to limit the invention disclosed herein.

27 EXAMPLE 1

28 An ethylene-methyl acrylate copolymer (manufactured by  
29 Chevron by the method disclosed in U.S. Patent  
30 No. 3,350,372) containing 20% by weight methyl acrylate  
31 (7.5 mole %) and having a melt index of 400 g/10 min.  
32 (190°C) was fed to a Werner & Pfleiderer corrosion-resistant

- 35 -

1 ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. The  
2 extruder had a ratio of length to diameter of about 44. The  
3 screw configuration for Examples 1-13 and Comparative  
4 Example A is given in Table 1 column A. Aqueous sodium  
5 hydroxide (50% NaOH by weight in all examples, except where  
6 noted otherwise) was fed to Zone 3 of the extruder at  
7 9.3 lbs./hr. The screw speed was 550 rpm.

8 The following extruder temperatures were measured:

9

Table 2

10	Zone No.	1	2	3	4	5	6	7
11	Temperature	236	350	253	253	230	245	260
12	(°C)							

13 Note: Zone 1: melting section for polymer to be reacted;  
14 Zone 2 & 3: reaction section;  
15 Zone 4: devolatilization section;  
16 Zones 5-7: extrusion section.

17 Water from the sodium hydroxide solution and the reaction  
18 by-product methanol were removed by a two-stage  
19 devolatilization. In all examples, the evolved water and  
20 methanol from the first devolatilization stage were  
21 condensed at atmospheric pressure. The second  
22 devolatilization stage was connected to a vacuum system in  
23 all examples. The second devolatilization stage had 28.4  
24 in. Hg vacuum during this run.

25 The reaction product was extruded through an eight-strand  
26 die, cooled on a stainless steel belt (about 20 feet in  
27 length, made by Sandvik) which was chilled by cold water  
28 underneath the belt, and subsequently pelletized.

29 The product had a melt flow rate of 0.33 g/10 min. (230°C).  
30 The product had a hydrolysis of 53% (i.e., 53% of the methyl

- 36 -

1 acrylate in the ethylene-methyl acrylate copolymer was  
2 converted to sodium acrylate).

3 The polymer was made into blown film on a Victor blown film  
4 line at the following processing conditions:

Table 3

Zone 1	Zone 2	Zone 3	Adapter	Die 1	Die 2	Die Pressure	Melt Temperature
400°F	440°F	515°F	435°F	430°F	440°F	7600 psi	440°F

8 The blown film had a thickness of 3.5 mils. The haze of the  
9 film was 2%, and the 60° gloss was 122. The 1% secant  
10 moduli of the film were 12,740 and 10,080 psi respectively  
11 for the machine direction (MD) and the transverse direction  
12 (TD).

13 All haze values were measured using the method of  
14 ASTM D 1003. The 60° gloss values were measured using the  
15 method of ASTM D 2457. The 1% secant modulus values and  
16 tensile strength values were measured using the method of  
17 ASTM D-638.

18 Melt index of feed resin was measured by the method of  
19 ASTM D 1239, using a temperature of 190°C and a 2.16 kg  
20 weight. The melt flow rate of a composition of this  
21 invention was determined by the method of ASTM D 1239 but  
22 using a temperature of 230°C rather than 190°C and using a  
23 2.16 kg weight.

24 The hydrolysis of the product is defined as the moles of  
25 metal salt of the alpha, beta-ethylenically-unsaturated  
26 carboxylic acid present in the product, expressed as a  
27 percentage of the moles of the ester of alpha,  
28 beta-ethylenically-unsaturated carboxylic acid present prior

- 37 -

1 to saponifying the copolymer. The terms "hydrolysis",  
2 "extent of hydrolysis", "percent hydrolysis", "percent  
3 saponified", and "extent of saponification" are used  
4 interchangeably.

5 The extent of hydrolysis is determined by dissolving 10 g.  
6 of ionomer in 250 ml. of tetrahydrofuran (THF) in a 500 ml.  
7 round-bottom flask, to which 1 ml. of glacial acetic acid is  
8 added. The flask is fitted with a refluxing condenser, and  
9 the contents are boiled for about 20 min. The mixture is  
10 poured into 1 liter of cold distilled water (about 15-20°C),  
11 and then filtered. The precipitate is subsequently washed  
12 with about 3 liters of distilled water. The precipitate is  
13 dried under vacuum, then weighed and dissolved in THF and  
14 titrated with 0.1 N potassium hydroxide in ethanol, using  
15 thymol blue to indicate the end-point of titration. The  
16 extent of hydrolysis is then calculated by dividing the  
17 moles of potassium used in titrating the sample by the moles  
18 of ester present in the initial ethylene-methyl acrylate  
19 copolymer prior to the saponification reaction.

20 EXAMPLE 2

21 The ethylene-methyl acrylate copolymer of Example 1 was fed  
22 to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin  
23 screw extruder at a rate of 100 lbs./hr. Aqueous sodium  
24 hydroxide was fed to Zone 3 of the extruder at a rate of  
25 11.2 lbs./hr. The screw speed was 500 rpm.

26 The following temperatures were measured during the process:

27 Table 4

28 Zone No.	1	2	3	4	5	6	7
29 Temperature 30 (°C)	271	252	255	256	230	231	241

- 38 -

1 The vacuum on the second devolatilization zone was 28.4 in.  
2 Hg. The reaction product was extruded, cooled on a Sandvik  
3 belt and pelletized in the same way as Example 1. The  
4 product had a melt flow rate of 0.20 g/10 min. (230°C). The  
5 hydrolysis of the product was 65%.

6 The polymer was made into blown film on a Victor blown film  
7 line using the processing conditions similar to those in  
8 Example 1. The haze of the blown film was 2%, and the 60°  
9 gloss was 133. The film had a tensile strength of 4010 and  
10 3180 psi respectively for MD and TD. The 1% secant moduli  
11 of the film were 14720 and 13110 psi respectively for MD and  
12 TD.

### 13 EXAMPLE 3

14 The ethylene-methyl acrylate copolymer of Example 1 was fed  
15 to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin  
16 screw extruder at a rate of 100 lbs./hr. Aqueous sodium  
17 hydroxide was fed to Zone 3 on the extruder at a rate of  
18 12.1 lbs./hr. The screw speed was 500 rpm.

19 The following temperatures were measured during the process:

20 Table 5

21 Zone No.	1	2	3	4	5	6	7
22 Temperature 23 (°C)	218	347	255	255	230	251	260

24 The vacuum on the second devolatilization zone was 28.5 in.  
25 Hg. The reaction product was extruded, cooled on a Sandvik  
26 belt and pelletized in the same way as Example 1. The  
27 product had a melt flow rate of 0.1 g/10 min. (230°C). The  
28 hydrolysis of the product was 70%.



- 39 -

The polymer was made into blown film on a Victor blown film line using the processing conditions similar to those in Example 1. The haze of the blown film was 2%, and the 60° gloss was 134. The film had a tensile strength of 4470 and 2420 psi respectively for MD and TD.

#### EXAMPLE 4

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 570 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3 on the extruder at a rate of 13.0 lbs./hr. The screw speed was 500 rpm.

The following temperatures were measured during the process:

Table 6

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	178	242	254	252	301	303	289

The vacuum on the second devolatilization zone was 25.5 in. Hg. The reaction product was extruded, cooled on a Sandvik belt and pelletized in the same way as Example 1. The product had a melt flow rate of 0.87 g/10 min. (230°C). The hydrolysis of the product was 69%.

The polymer was made into blown film on a Victor blown film line using the processing conditions similar to those in Example 1. The haze of the blown film was 2%, and the 60° gloss (ASTM D 2457) was 135. The film had a tensile strength of 2870 and 1760 psi respectively for MD and TD.

- 40 -

EXAMPLE 5

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 440 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3 on the extruder at a rate of 13.0 lbs./hr. The screw speed was 500 rpm.

The following temperatures were measured during the process:

Table 7

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	189	257	257	258	251	263	283

The vacuum on the second devolatilization zone was 28.4 in. Hg. The reaction product was extruded, cooled on a Sandvik belt and pelletized in the same way as Example 1. The product had a melt flow rate of 0.81 g/10 min. (230°C). The hydrolysis of the product was 72%.

The polymer was made into blown film on a Victor blown film line using the processing conditions similar to those in Example 1. The haze of the blown film was 2%, and the 60° gloss was 135. The film had a tensile strength of 2600 and 1850 psi respectively for MD and TD.

EXAMPLE 6

An ethylene-methyl acrylate copolymer containing 23% by weight methyl acrylate and having a melt index of 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3

- 41 -

1 on the extruder at a rate of 10.7 lbs./hr. The screw speed  
2 was 500 rpm.

3 The following temperatures were measured during the process:

Table 8

4 Zone No.	1	2	3	4	5	6	7
5 Temperature 6 (°C) 7	181	247	256	255	255	254	270

8 The vacuum on the second devolatilization zone was 26.7 in.  
9 Hg. The reaction product was extruded, cooled on a Sandvik  
10 belt and pelletized in the same way as Example 1. The  
11 product had a melt flow rate of 0.54 g/10 min. (230°C). The  
12 hydrolysis of the product was 51%.

13 The polymer was made into blown film on a Victor blown film  
14 line using the processing conditions similar to those in  
15 Example 1. The haze of the blown film was 2%, and the 60°  
16 gloss was 124. The film had a tensile strength of 2270 and  
17 1470 psi respectively for MD and TD.

#### 18 EXAMPLE 7

19 An ethylene-methyl acrylate copolymer containing 23% by  
20 weight methyl acrylate and having a melt index of  
21 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer  
22 corrosion-resistant ZSK-40mm twin screw extruder at a rate  
23 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3  
24 on the extruder at a rate of 12.8 lbs./hr. The screw speed  
25 was 500 rpm.

- 42 -

1 The following temperatures were measured during the process:

Table 9

3 Zone No.	1	2	3	4	5	6	7
4 Temperature 5 (°C)	175	247	253	259	254	257	271

6 The vacuum on the second devolatilization zone was 26.6 in.  
7 Hg. The reaction product was extruded, cooled on a Sandvik  
8 belt and pelletized in the same way as Example 1. The  
9 product had a melt flow rate of 0.45 g/10 min. (230°C). The  
10 hydrolysis of the product was 61%.

11 The polymer was made into blown film on a Victor blown film  
12 line using the processing conditions similar to those in  
13 Example 1. The haze of the blown film was 3%, and the 60°  
14 gloss was 132. The film had a tensile strength of 2730 and  
15 1960 psi respectively for MD and TD.

#### 16 EXAMPLE 8

17 An ethylene-methyl acrylate copolymer containing 23% by  
18 weight methyl acrylate and having a melt index of  
19 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer  
20 corrosion-resistant ZSK-40mm twin screw extruder at a rate  
21 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3  
22 on the extruder at a rate of 9.6 lbs./hr. The screw speed  
23 was 500 rpm.

24 The following temperatures were measured during the process:

Table 10

26 Zone No.	1	2	3	4	5	6	7
27 Temperature 28 (°C)	193	284	257	259	254	254	271

- 43 -

1 The vacuum on the second devolatilization zone was 26.2 in.  
2 Hg. The reaction product was extruded, cooled on a Sandvik  
3 belt and pelletized in the same way as Example 1. The  
4 product had a melt flow rate of 0.60 g/10 min. (230°C). The  
5 hydrolysis of the product was 46%.

6 The polymer was made into blown film on a Victor blown film  
7 line using the processing conditions similar to those in  
8 Example 1. The haze of the blown film was 2%, and the 60°  
9 gloss was 120. The film had a tensile strength of 1950 and  
10 1240 psi respectively for MD and TD.

#### 11 EXAMPLE 9

12 An ethylene-methyl acrylate copolymer containing 22% by  
13 weight methyl acrylate and having a melt index of  
14 470 g/10 min. (190°C) was fed to the Werner & Pfleiderer  
15 corrosion-resistant ZSK-40mm twin screw extruder at a rate  
16 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3  
17 on the extruder at a rate of 14.3 lbs./hr. The screw speed  
18 was 500 rpm.

19 The following temperatures were measured during the process:

20 Table 11

21 Zone No.	1	2	3	4	5	6	7
22 Temperature 23 (°C)	298	326	255	266	254	254	271

24 The vacuum on the second devolatilization zone was 28.4 in.  
25 Hg. The reaction product was extruded, cooled on a Sandvik  
26 belt and pelletized in the same way as Example 1. The  
27 product had a melt flow rate of 0.23 g/10 min. (230°C). The  
28 hydrolysis of the product was 70%.

- 44 -

1 The polymer was made into blown film on a Victor blown film  
2 line using the processing conditions similar to those in  
3 Example 1. The haze of the blown film was 1%, and the 60°  
4 gloss was 134. The film had a tensile strength of 3000 and  
5 2170 psi respectively for MD and TD.

#### 6 EXAMPLE 10

7 An ethylene-methyl acrylate copolymer containing 23% by  
8 weight methyl acrylate and having a melt index of  
9 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer  
10 corrosion-resistant ZSK-40mm twin screw extruder at a rate  
11 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3  
12 on the extruder at a rate of 8.6 lbs./hr. The screw speed  
13 was 500 rpm.

14 The following temperatures were measured during the process:

15 Table 12

16 Zone No.	1	2	3	4	5	6	7
17 Temperature 18 (°C)	177	262	255	253	254	255	270

19 The vacuum on the second devolatilization zone was 25.8 in.  
20 Hg. The reaction product was extruded, cooled on a Sandvik  
21 belt and pelletized in the same way as Example 1. The  
22 product had a melt flow rate of 1.25 g/10 min. (230°C). The  
23 hydrolysis of the product was 41%.

24 The polymer was made into blown film on a Victor blown film  
25 line using the processing conditions similar to those in  
26 Example 1. The haze of the blown film was 4%, and the 60°  
27 gloss was 104. The film had a tensile strength of 1910 and  
28 970 psi respectively for MD and TD.

- 45 -

EXAMPLE 11

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 100 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3 on the extruder at a rate of 4.7 lbs./hr. The screw speed was 500 rpm.

The following temperatures were measured during the process:

Table 13

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	253	322	254	230	230	231	241

The vacuum on the second devolatilization zone was 28.4 in. Hg. The reaction product was extruded, cooled on a Sandvik belt and pelletized in the same way as Example 1. The product had a melt flow rate of 0.67 g/10 min. (230°C). The hydrolysis of the product was 26%.

The polymer was made into blown film on a Victor blown film line using the processing conditions similar to those in Example 1. The haze of the blown film was 3%, and the 60° gloss was 115. The film had a tensile strength of 1150 and 1080 psi respectively for MD and TD.

EXAMPLE 12

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 400 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3

- 46 -

1 on the extruder at a rate of 9.3 lbs./hr. The screw speed  
2 was 500 rpm.

3 The following temperatures were measured during the process:

Table 14

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	209	201	266	255	256	256	256

8 The vacuum on the second devolatilization zone was 24.7 in.  
9 Hg. The reaction product was extruded, cooled in a water  
10 bath, and pelletized. The pellets were dried in a vacuum  
11 over at 65°C and 29.5 in. Hg for 48 hours. The product had  
12 a melt flow rate of 0.66 g/10 min. (230°C). The hydrolysis  
13 of the product was 49%.

14 The polymer was made into blown film on a Victor blown film  
15 line using the processing conditions similar to those in  
16 Example 1. The haze of the blown film was 3%, and the 60°  
17 gloss was 128.

#### 18 EXAMPLE 13

19 An ethylene-methyl acrylate copolymer containing 20% by  
20 weight methyl acrylate and having a melt index of  
21 150 g/10 min. (190°C) was fed to the Werner & Pfleiderer  
22 corrosion-resistant ZSK-40mm twin screw extruder at a rate  
23 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3  
24 on the extruder at a rate of 7.4 lbs./hr. The screw speed  
25 was 450 rpm.



- 47 -

1 The following temperatures were measured during the process:

Table 15

2 Zone No.	1	2	3	4	5	6	7
3 Temperature	188	199	276	253	257	260	262
4 (°C)							

6 The vacuum on the second devolatilization zone was 28.5 in.  
7 Hg. The reaction product was extruded, cooled in a water  
8 bath, and pelletized. The pellets were dried in a vacuum  
9 over at 65°C and 29.5 in. Hg for 48 hours. The product had  
10 a melt flow rate of 0.22 g/10 min. (230°C). The hydrolysis  
11 of the product was 42%.

12 The polymer was made into blown film on a Victor blown film  
13 line using the processing conditions similar to those in  
14 Example 1. The haze of the blown film was 4%, and the 60°  
15 gloss was 122.

#### 16 EXAMPLE 14

17 An ethylene-methyl acrylate copolymer containing 20% by  
18 weight methyl acrylate and having a melt index of  
19 400 g/10 min. (190°C) was fed to a Werner & Pfleiderer  
20 ZSK-58mm twin screw extruder at a rate of 425 lbs./hr. The  
21 screw was configured to provide substantially the same  
22 mixing as provided in the ZSK-40mm extruder in Examples 1-  
23 13. Aqueous sodium hydroxide was fed to the reaction zone  
24 on the extruder at a rate of 56 lbs./hr.

25 The screw speed of the extruder was at 500 rpm. The  
26 temperatures in the reaction zones were 226°C to 338°C. The  
27 product was 71% hydrolyzed. The product had similar optical  
28 properties to the product of Example 3.

- 48 -

EXAMPLE 15

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 400 g/10 min. (190°C) was fed to a Werner & Pfleiderer ZSK-70mm twin screw extruder at a rate of 450 lbs./hr. The screw was configured to provide substantially the same mixing as provided in the ZSK-40mm extruder in Examples 1-13. Aqueous sodium hydroxide was fed to the reaction zone on the extruder at a rate of 50 lbs./hr.

The screw speed of the extruder was at 580 rpm. The temperatures in the reaction zones were 330°C to 350°C. The product was 61% hydrolyzed. The product had similar optical properties to the product of Example 3.

COMPARATIVE EXAMPLE A

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 20 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3 on the extruder at a rate of 4.6 lbs./hr. The screw speed was 400 rpm.

The following temperatures were measured during the process:

Table 16

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	216	213	270	269	270	271	270

The vacuum on the second devolatilization zone was 27.9 in. Hg. The reaction product was extruded, cooled in a water bath, and pelletized. The pellets were dried in a vacuum oven at 65°C and 29.5 in. Hg for 48 hours. The product had

- 49 -

1 a melt flow rate of 3.2 g/10 min. (190°C). The hydrolysis  
2 of the product was 15%.

3 The polymer was made into blown film on a Victor blown film  
4 line using the processing conditions similar to those in  
5 Example 1. The haze of the blown film was 81%, and the 60°  
6 gloss was 35.

7 This Comparative Example A shows that saponifying 15% of the  
8 methyl acrylate groups to form the sodium salt of acrylic  
9 acid is insufficient at these reaction conditions to produce  
10 the low haze of compositions of this invention.

11 COMPARATIVE EXAMPLE B

12 An ethylene-methyl acrylate copolymer containing 20% methyl  
13 acrylate by weight and having a melt index of 400 g/10 min.  
14 was fed to a Werner & Pfleiderer ZSK-30 corrosion-resistant  
15 extruder at 13.2 lbs/hr. 1.73 lbs/hr. of 35% sodium  
16 hydroxide solution was fed to zone 3 of the extruder. The  
17 extruder had the configuration of elements shown in Table 1  
18 column B.

19 The following extruder temperatures were measured:

20 Table 17

21 Zone No.	1	2	3	4	5	6	7
22 Temperature	230	275	275	275	275	240	235
23 (°C)							

24 Water and the by-product methanol were removed in a two-  
25 stage devolatilization zone. The polymer strands were  
26 cooled in a water bath and pelletized. The pellets were  
27 vacuum-dried overnight at about 25 in. Hg vacuum and at  
28 68°C.

- 50 -

1 Chemical analysis of the product indicated a degree of  
2 saponification of 49.2%. The product had a melt index  
3 (190°C) of 0.54 g/10 min.

4 A 1/2 inch Randcastle miniextruder was used to make a cast  
5 film of about 4 inch width. The temperature at the feed  
6 zone and barrels 1A through 3A was 430°C, while the die  
7 temperature was 440°C. The film had a haze of 55% and a 60°  
8 gloss of 20.

9 It is believed that the poor clarity of this example results  
10 from a more dilute caustic solution and poorer mixing at  
11 these reaction conditions as compared to the conditions  
12 which produce compositions of this invention.

13 COMPARATIVE EXAMPLE C

14 An ethylene-methyl acrylate copolymer containing 20% methyl  
15 acrylate by weight and having a melt index of 400 g/10 min.  
16 was fed to a Werner & Pfleiderer ZSK-30 corrosion-resistant  
17 extruder at 13.2 lbs/hr. 2.29 lbs/hr. of 35% sodium  
18 hydroxide solution was fed to zone 3 of the extruder. The  
19 extruder had the configuration of elements shown in Table 1  
20 column B.

21 The following extruder temperatures were measured:

22 Table 18

23 Zone No.	1	2	3	4	5	6	7
24 Temperature 25 (°C)	230	275	275	275	275	240	235

26 Water and the by-product methanol were removed in a two-  
27 stage devolatilization zone. The polymer strands were  
28 cooled in a water bath and pelletized. The pellets were

- 51 -

1 vacuum-dried overnight at about 25 in. Hg vacuum and at  
2 68°C.

3 Chemical analysis of the product indicated a degree of  
4 saponification of 65.2%. The product had a melt flow rate  
5 of 0.38 g/10 min. (230°C).

6 A 1/2 inch Randcastle miniextruder was used to make a cast  
7 film of about 4 inch width. The temperature at the feed  
8 zone and barrels 1A through 3A was 430°C, while the die  
9 temperature was 440°C. The film had a haze of 15% and a 60°  
10 gloss of 66.

11 This comparative example shows that a greater extent of  
12 hydrolysis provided clearer ionomer, but mixing conditions  
13 as supplied by the screw design of Table 1 column B when  
14 using 35% aqueous caustic did not appear to provide the  
15 intensive mixing and reaction conditions necessary to obtain  
16 a haze of 10% or less.

17 COMPARATIVE EXAMPLE D

18 Ethylene-methyl acrylate copolymer having 20 weight percent  
19 methyl acrylate and a 400 melt index (190°C) was saponified  
20 with a 35% by weight aqueous solution of sodium hydroxide  
21 per the method of Comparative Example B. The product was  
22 60% saponified and had a melt index (190°C) of 0.06. The  
23 tensile strength in the machine direction was 1582 psi.

24 COMPARATIVE EXAMPLE E

25 Ethylene-methyl acrylate copolymer having 25 weight percent  
26 methyl acrylate and a 457 melt index (190°C) was saponified  
27 with a 35% by weight aqueous solution of sodium hydroxide  
28 per the method of Comparative Example B. The product was  
29 44% saponified and had a melt index (190°C) of 0.04. The  
30 tensile strength in the machine direction was 985 psi.

- 52 -

EXAMPLE 16 -- ACID BATH COOLING OF IONOMER

26.4 lbs./hr. of the ethylene-methyl acrylate copolymer of Example 1 were fed to a Werner & Pfleiderer corrosion resistant ZSK-30 twin-screw extruder having the configuration of elements given in Table 1 column C. 50% aqueous sodium hydroxide was fed into zone 3 at 2.5 lb./hr. The screw speed was 500 rpm.

The following extruder temperatures were measured:

Table 19

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	174	200	255	260	254	267	255

Volatile components were removed in a two port devolatilization section, and the second port had a vacuum of 28 in. Hg. The polymer strands from a four-strand die were cooled in a 5% phosphoric acid bath which was 10 ft. long, and were then rinsed in a 2 ft. water bath and pelletized in a Conair pelletizer.

During 1.75 hours of operation, the ionomer was efficiently cooled and pelletized, and the acid bath remained acidic and clear with no evidence of dissolved polymer. Total carbon analysis of the cooling water (determined by potentiometric titration) at the end of operation showed less than 20 ppm of dissolved carbon. By contrast, when the same polymer was cooled in water, the water bath became turbid and milky-white within a few minutes of operation.

The resulting pellets were colorless, shiny, and clear.

EXAMPLE 17

- 53 -

1 This example shows a copolymer of ethylene, methyl acrylate,  
2 sodium acrylate, and acrylic acid. First, ethylene-methyl  
3 acrylate copolymer having 20 weight percent methyl acrylate  
4 and 153 melt index (190°C) was saponified in a Werner-  
5 Pfleiderer ZSK-30 twin-screw reactive extruder using 50%  
6 aqueous sodium hydroxide and substantially the same reaction  
7 conditions as Example 16. The extent of saponification was  
8 42%. The pelletized ionomer was clear and glossy and had a  
9 melt flow rate (230°C) of 0.17 g/10 min.

10 The ionomer pellets were fed to the extruder at a rate of 12  
11 kg/hr. 85.6% aqueous phosphoric acid was fed to Zone 3 of  
12 the extruder at a rate of 0.14 kg/hr., and the product was  
13 extruded, cooled in a water bath, and pelletized.

14 The product retained its clear and glossy optical  
15 properties, and the melt flow rate increased to 1.0 g/10  
16 min. (230°C). Film that was made on the Randcastle mini-  
17 extruder had a tensile strength in the machine direction of  
18 2418 psi.

19 EXAMPLE 18

20 Ethylene-methyl acrylate copolymer having 20 weight percent  
21 methyl acrylate and 400 melt index (190°C) was saponified in  
22 a ZSK-30 extruder having the configuration of elements given  
23 in Table 1 column C with 50% aqueous sodium hydroxide at a  
24 reaction temperature of about 148°C. The screw speed was  
25 500 rpm. The copolymer was fed to the extruder at a rate of  
26 12 kg/hr., and the product was about 54% saponified. The  
27 product was visually clear.

28 COMPARATIVE EXAMPLE F

29 Ethylene-methyl acrylate copolymer having 20 weight percent  
30 methyl acrylate and 400 melt index (190°C) was saponified  
31 with 50% aqueous sodium hydroxide in a ZSK-30 extruder

- 54 -

1 having the configuration of screw elements given in Table 1  
2 column B at a reaction temperature of about 149°C. The  
3 screw speed was 500 rpm. The copolymer was fed to the  
4 extruder at a rate of 16 kg/hr., and the product was about  
5 52% saponified. The product was visually cloudy.

6 This example shows that insufficient mixing was supplied by  
7 the screw configuration of Table 1 column B at these  
8 reaction conditions.

#### 9 EXAMPLE 19

10 26.4 lbs./hr. of the ethylene-methyl acrylate copolymer of  
11 Example 1 were fed to a Werner & Pfleiderer corrosion  
12 resistant ZSK-30 twin-screw extruder having the  
13 configuration of elements given in Table 1 column C. 50%  
14 aqueous potassium hydroxide was fed into zone 3 at the rate  
15 given in Table 20. The screw speed was 500 rpm.

16 The extruder temperatures were substantially the same as  
17 those given in Table 19. Volatile components were removed  
18 in a two port devolatilization section, and the second port  
19 had a vacuum of 28 in. Hg. The following table summarizes  
20 the feed rate of potassium hydroxide, the melt flow rate  
21 (230°C), and the extent of saponification of the methyl  
22 acrylate groups.

23 TABLE 20

24	25	26	27	28	29	30	31
Feed rate (lb./hr.) of 50% aqueous potassium hydroxide				Melt flow rate of ionomer of this Example		Extent of saponification	
1.87				1.66		27	
2.62				0.60		37	
3.74				0.23		53	
5.28				0.07		78	



- 55 -

COMPARATIVE EXAMPLE G

An ethylene-methyl acrylate copolymer containing 20% methyl acrylate by weight and having a melt index of 20 g/10 min. (190°C) was fed to a Werner & Pfleiderer ZSK-40 corrosion-resistant extruder at 100 lbs/hr. 4.7 lbs/hr. of 50% sodium hydroxide solution was fed to zone 3 of the extruder. The screw speed was 275 rpm.

The following extruder temperatures were measured:

Table 21

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	200	208	279	280	278	280	281

The vacuum on the second devolatilization zone was 27.0 in. Hg. The reaction product was extruded, cooled in a water bath, and pelletized. The pellets were dried in a vacuum oven at 65°C and 29.5 in. Hg for 48 hours. The product had a melt index of 1.6 g/10 min. (190°C). The hydrolysis of the product was 24%.

The polymer was made into blown film on a Victor blown film line using the processing conditions similar to those in Example 1. The haze of the blown film was 97%, and the 60° gloss was 43.

The SEM micrograph shown in Figure 2 was taken on a freeze-fractured surface of the blown film made from this ionomer.

EXAMPLE 20

Ethylene-methyl acrylate copolymer having 20% by weight methyl acrylate and a melt index of 20 g/10 min. (190°C) was 25% hydrolyzed by the method of Comparative Example A, and

- 56 -

1 this sodium ionomer was ground to 60 mesh-sized powder. 10  
2 grams of the ground ionomer were put into a 500 ml single-  
3 neck round-bottom flask, and 250 ml of stabilized THF and a  
4 magnetic stirrer were added. The above mixture was heated  
5 to reflux and stirred for about 10 minutes to ensure that  
6 the ionomer dissolved. After dissolution, 1.6 ml of 2 N  
7 aqueous hydrochloric acid was added to the flask. The  
8 reaction continued for 2 hours, then the solution was  
9 precipitated in 1 liter of cold water, filtered, and dried  
10 under vacuum.

11 The reaction produced 9.7 grams of white polymer precipitate  
12 having a melt index of 0.9 g/10 min. (190°C). Fourier-  
13 transform infrared (FT-IR) analysis showed that the  
14 carboxylic acid group was present (1708  $\text{cm}^{-1}$ , absorbance  
15 1.5259) as well as sodium acrylate (1558  $\text{cm}^{-1}$ , absorbance  
16 1.0294). This indicated that 60% of the sodium acrylate  
17 groups present in the ionomer prior to acidification was  
18 converted to acid groups, thus giving a stoichiometric  
19 reaction of this acid with sodium acrylate. The acidified  
20 ionomer was a tetrapolymer of ethylene, methyl acrylate,  
21 sodium acrylate, and acrylic acid having about 5.7 mole  
22 percent methyl acrylate, 0.8 mole percent sodium acrylate,  
23 and 1.1 mole percent acrylic acid. The melt index of the  
24 acidified ionomer was 6.3 g/10 min. (190°C).

25 The acidified ionomer had excellent adhesion to a polar  
26 substrate such as unprimed aluminum foil. Both non-  
27 acidified ionomer and acidified ionomer were separately  
28 pressed between two pieces of unprimed aluminum foil in a  
29 hydraulic press having two heated plates. The pellets and  
30 foil were heated without pressure for about 5 minutes at  
31 350°C, then the pressure was increased to 20,000 psi and  
32 maintained for an additional 5 minutes at 350°C. The

- 57 -

1 acidified ionomer sealed the aluminum foil and could not be  
2 separated from it without tearing the foil. The non-  
3 acidified ionomer was easily peeled from the foil.

4 Separate films of acidified ionomer and non-acidified  
5 ionomer were each made by placing 0.2 g of the ionomer  
6 between two pieces of Mylar film. The ionomer was heated  
7 and pressed as above. The Mylar was separated from the  
8 ionomer with a small amount of acetone. The acidified  
9 ionomer film was clear, having no observable haze and having  
10 an observable high gloss. The non-acidified ionomer film  
11 was opaque, dull, and frosty.

#### 12 EXAMPLE 21

13 Example 20 was repeated, except that 0.2556 g of glacial  
14 acetic acid was substituted in place of the hydrochloric  
15 acid. The reaction produced 9.8 grams of acidified ionomer  
16 as a white precipitate. FT-IR analysis indicated that 80%  
17 of the sodium acrylate present in the ionomer prior to  
18 acidification were converted to acid groups. The acidified  
19 ionomer was a tetrapolymer of ethylene, methyl acrylate,  
20 sodium acrylate, and acrylic acid, having about 5.7 mole  
21 percent methyl acrylate, 0.4 mole percent sodium acrylate,  
22 and 1.5 mole percent acrylic acid in the acidified ionomer.  
23 The acidified ionomer had a melt index of 11.7 g/10 min.  
24 (190°C).

25 The acidified ionomer produced a clear film with no  
26 observable haze and observably high gloss. The non-  
27 acidified ionomer produced opaque, dull, and frosty film.  
28 The acidified ionomer also exhibited excellent adhesion to  
29 aluminum foil, particularly when compared to the non-  
30 acidified ionomer.

#### 31 EXAMPLE 22

- 58 -

An ethylene-methyl acrylate copolymer having 20 weight percent methyl acrylate and a melt index of 153 g/10 min. (190°C) was 35% hydrolyzed by the method of Comparative Example A. The melt index of this ionomer was 9.7 g/10 min. (190°C), and the haze of a cast film was 98%, the 60° gloss was 6, and the tear strength (g/mil) in the machine direction was 33 and in the transverse direction was 41.

This ionomer was fed continuously at a rate of 10 kg/hr to the Werner-Pfleiderer ZSK-30 extruder which was maintained at 210°C. Primacor Grade 3330 was also fed continuously to the extruder in the ratio given below, and the properties of a cast film of the acidified copolymer made on the Randcastle mini-extruder are listed in Table 22.

Table 22

Kg. Primacor per Kg. Ionomer	Melt index (g/10 min. @ 190°C	Haze (%)	60° gloss	Tear strength, g/mil, machine direction	Tear strength g/mil, trans- verse direc- tion
0.076	6.6	48	18	26	21
0.152	5.6	70	11	24	38
0.228	4.3	82	9	18	57

EXAMPLE 23

The non-acidified ionomer of Example 22 was fed continuously to the extruder at a rate of 8 kg/hr. and was acidified using 21.5% phosphoric acid, as detailed below. The properties of a cast film of the acidified copolymer made on the Randcastle mini-extruder are listed in Table 23.

- 59 -

Table 23

Kg H <sub>3</sub> PO <sub>4</sub> (21.5%) / kg. ionomer	Melt index (190°C)	Haze (%)	60° glöss	Tear strength (g/mil), machine direction	Tear strength (g/mil), trans- verse direc- tion
0.0375	8.0	46	18	28	36
0.0738	20.0	23	51	45	43
0.1113	36.3	23	51	71	49
0.1488	57.3	32	35	79	70

Tear strength was measured using the method of ASTM D-1922.

EXAMPLE 24

An ethylene-methyl acrylate copolymer having 20 weight percent methyl acrylate was saponified substantially by the method of Example 1. The percent hydrolysis and properties of the polymer are listed in the following Table 24.

- 60 -

TABLE 24

% HYDRO- LYZED	% HAZE	60° GLOSS	TENSILE STRENGTH, psi		1° SECANT MODULUS, psi		MELT POINT TEMP. °C	ELMENDORF TEAR STRENGTH, g/mil		ELONGA- TION @ BREAK, %	
			MD	TD	MD	TD		MD	TD	MD	TD
35	13.3	55	1709	1445	7893	7667	77	12	14	350	376
42	1.4	126	2081	1928	14831	14054	76	17	24	420	434
50	0.5	140	2321	1984	8193	7718	73	26	22	365	405

Melt point temperature was measured using a differential scanning calorimeter and standard methods well-known in the art.

Elmendorf tear strength was measured using ASTM D-1922.

Elongation at break was measured using ASTM D-882.

- 61 -

The hot tack strength for these ionomers is summarized in Figure 3.

EXAMPLE 25

Samples of ethylene methyl acrylate copolymer having the methyl acrylate contents in following Table 25 were saponified to various degrees of hydrolysis using substantially the method of Example 1. In addition, ethylene methyl acrylate copolymers made by the method of U.S. Ser. No. 07/947,870, filed Sep. 21, 1992, where all of the methyl acrylate was fed to a first reaction zone of a multi-zone high-pressure polymerization reactor, were saponified to various degrees of hydrolysis. Table 25 summarizes the melt point temperatures of these ionomers.

Table 25

WT. % METHYL ACRYLATE	ETHYLENE METHYL ACRYLATE COPOLYMER MADE BY METHOD OF U.S. 3,350,372		ETHYLENE METHYL ACRYLATE COPOLYMER MADE BY METHOD OF U.S. SER. NO. 07/947,870	
	% HYDROLYZED	MELT POINT TEMP., °C	% HYDROLYZED	MELT POINT TEMP., °C
12	62	90	60	97
12	86	83	83	99
12	--	--	83	98
12	100	87	99	93
20	--	--	35	92
20	47	87	42	91
20	51	86	50	91
20	61	83	65	92
20	72	64	--	--
24	42	64	--	--

- 62 -

EXAMPLE 26

1 Ionomer was made substantially by the method of Example 1.  
2 This ionomer was cast coextruded individually with three  
3 polymers on a Randcastle Mini-Extruder to form three 2-layer  
4 films, where each layer was 2 mil thick. Adhesion strength  
5 of the 2-layer films was analyzed using TAPPI Uniform Method  
6 541, "Adhesion to Non-Porous Flexible Substrates", which is  
7 incorporated by reference in its entirety herein.  
8 Ionomer/propylene film (Fina 3275) had an adhesion of 770  
9 g/inch; ionomer/high density polyethylene (Chevron HiD®  
10 9650) could not be separated; and ionomer/nylon (Allied  
11 Chemical's Capron 8350) had an adhesion of 80 g/inch.  
12

13 The heat seal strength of the ionomer/polyethylene film  
14 above is summarized in Figure 4.

EXAMPLE 27

15 Ethylene-methyl acrylate-butyl acrylate copolymer containing  
16 10 weight percent methyl acrylate and 10 weight percent  
17 butyl acrylate is about 50% hydrolyzed substantially by the  
18 method of Example 1. This yields an ethylene-methyl  
19 acrylate-butyl acrylate-sodium acrylate copolymer. It is  
20 expected that the methyl acrylate reacts at a faster rate  
21 than the butyl acrylate, so more methyl acrylate is  
22 converted to the sodium salt than butyl acrylate. This  
23 product is useful in applications where a higher melt-point  
24 temperature is desired, such as films or bags which contact  
25 hot food or liquids.  
26



- 63 -

## 1 WE CLAIM:

2 1. A method of making an ionomer composition comprising:

3 A) contacting:

4 (1) a Group IA metal-containing solution with

5 (2) a molten or fluid copolymer comprising alpha-  
6 olefins having from two to eight carbon atoms  
7 and esters of alpha, beta-ethylenically-  
8 unsaturated carboxylic acids having from four  
9 to twenty two carbon atoms and having a melt  
10 index between about 100 and about 2000 g/10  
11 min., as measured by ASTM method D 1239 at  
12 190°C; and13 B) intensively mixing the copolymer and Group IA  
14 metal-containing solution at a temperature and to  
15 an extent which provides an ionomer composition  
16 having no more than ten percent haze.17 2. The method of claim 1 wherein the copolymer comprises  
18 ethylene methyl acrylate copolymer.19 3. The method of claim 1 or 2 wherein said copolymer has a  
20 melt index between 300 and 600 g/10 min.21 4. The method of any of claims 1-3 wherein the Group IA  
22 metal-containing solution comprises aqueous metal  
23 hydroxide, where the metal is selected from the group  
24 consisting of sodium and potassium.25 5. The method of claim 4 wherein the concentration of  
26 metal hydroxide in the aqueous metal hydroxide is at  
27 least 50 percent by weight.28 6. The method of any of claims 1-5 wherein the intensive  
29 mixing is provided by a twin-screw extruder.

- 64 -

- 1        7.    The method of any of claims 1-6 wherein the intensive  
2           mixing occurs at a temperature between 200 and 350°C.
- 3        8.    The method of claim 7 wherein the temperature is  
4           between 275 and 350°C.
- 5        9.    The method of any of claims 1-8 wherein the intensive  
6           mixing provides an ionomer composition substantially  
7           free of ionic clusters greater than 0.05 micron in  
8           size.
- 9        10.   A composition made by the method of any of claims 1-9.
- 10       11.   A composition comprising a copolymer of alpha-olefins  
11           having from two to eight carbon atoms, esters of alpha,  
12           beta-ethylenically-unsaturated carboxylic acids having  
13           from four to twenty-two carbon atoms, and metal salts  
14           of acrylic or methacrylic acid, wherein said copolymer  
15           has a haze of no more than ten percent as measured by  
16           ASTM method D 1003.
- 17       12.   The composition of claim 10 or 11 having a haze of no  
18           more than seven percent.
- 19       13.   The composition of claim 12 having a haze of no more  
20           than five percent.
- 21       14.   The composition of claim 13 having a haze of no more  
22           than two percent.
- 23       15.   The composition of any of claims 10-14 wherein the  
24           alpha-olefin consists essentially of ethylene.

- 65 -

- 1      16. The composition of any of claims 10-15 wherein the  
2      metal of said metal salt is selected from the group  
3      consisting of sodium, lithium, and potassium.
- 4      17. The composition of any of claims 10-16 wherein said  
5      ester comprises methyl acrylate.
- 6      18. The composition of any of claims 10-17 wherein the  
7      metal of said metal salt consists essentially of  
8      sodium.
- 9      19. The composition of any of claims 10-18 wherein said  
10     metal salt of acrylic or methacrylic acid comprises  
11     between about 1.9 and about 7.5 mole percent of said  
12     copolymer.
- 13     20. The composition of any of claims 10-19 wherein said  
14     esters of alpha, beta-ethylenically-unsaturated  
15     carboxylic acid comprise between about 2.3 and about  
16     7.4 mole percent of said copolymer.
- 17     21. The composition of any of claims 10-20 wherein said  
18     alkali metal salt of alpha, beta-ethylenically-  
19     unsaturated carboxylic acid comprises between about 3.0  
20     and about 6.5 mole percent of said copolymer.
- 21     22. The composition of any of claims 10-21 wherein said  
22     esters of alpha, beta-ethylenically-unsaturated  
23     carboxylic acid comprise between about 2.8 and about  
24     6.3 mole percent of said copolymer.
- 25     23. The composition of any of claims 10-22 wherein the  
26     composition is acidified.

- 66 -

- 1      24. The composition of claim 23 wherein the acid is a  
2      polymeric acid.
- 3      25. The composition of claim 23 wherein the acid is  
4      phosphoric acid.
- 5      26. The composition of any of claims 10-25 wherein the  
6      composition has a 60° gloss of at least 100.
- 7      27. A film comprising the composition of any of claims 10-  
8      26.
- 9      28. The film of claim 27 having a thickness of no more than  
10      about 0.5 mil.
- 11     29. A blow-molded article comprising the composition of any  
12     of claims 10-25.
- 13     30. An easy-open package comprising the composition of any  
14     of claims 10-25.
- 15     31. The composition of any of claims 10-26 wherein a  
16     strand, pellet, or film of the composition is acidified  
17     on its surface.
- 18     32. A method of reducing the water solubility of an ionomer  
19     composition formed into a shape such as strands,  
20     pellets, or film comprising contacting a surface of the  
21     shape with an acid.
- 22     33. The method of claim 32 wherein the acid comprises a  
23     non-oxidizing acid.
- 24     34. The method of claim 33 wherein the acid consists  
25     essentially of a dilute aqueous solution of an acid

- 67 -

1 chosen from the group consisting of phosphoric acid,  
2 hydrochloric acid, and acetic acid.

3 35. A method for reducing the haze of a copolymer  
4 comprising combining:  
5 A) acid; and  
6 B) a copolymer of alpha-olefins having from two to  
7 eight carbon atoms, esters of alpha, beta-  
8 ethylenically-unsaturated carboxylic acids having  
9 from four to twenty-two carbon atoms, and metal  
10 salts of acrylic or methacrylic acid, wherein said  
11 copolymer has a haze of greater than ten percent  
12 as measured by ASTM method D 1003  
13 and uniformly mixing the copolymer and acid in an  
14 amount and at conditions sufficient to reduce the haze  
15 of a film.

16 36. A method for reducing the haze and increasing the melt  
17 index of a copolymer comprising combining:  
18 A) acid; and  
19 B) a copolymer of alpha-olefins having from two to  
20 eight carbon atoms, esters of alpha, beta-  
21 ethylenically-unsaturated carboxylic acids having  
22 from four to twenty-two carbon atoms, and metal  
23 salts of acrylic or methacrylic acid, wherein said  
24 copolymer has a haze of greater than ten percent  
25 as measured by ASTM method D 1003  
26 and uniformly mixing the copolymer and acid in an  
27 amount and at conditions sufficient to reduce the haze  
28 of a pressed film.

29 37. A method for reducing the haze and increasing the  
30 adhesion of a copolymer comprising combining:  
31 A) acid; and

- 68 -

- 1           B)   a copolymer of alpha-olefins having from two to  
2               eight carbon atoms, esters of alpha, beta-  
3               ethylenically-unsaturated carboxylic acids having  
4               from four to twenty-two carbon atoms, and metal  
5               salts of acrylic or methacrylic acid, wherein said  
6               copolymer has a haze of greater than ten percent  
7               as measured by ASTM method D 1003  
8           and uniformly mixing the copolymer and acid in an  
9           amount and at conditions sufficient to reduce the haze  
10          of a pressed film.
- 11       38.   The method of any of claims 35-37 wherein the copolymer  
12           and acid are mixed in an extruder.
- 13       39.   The method of any of claims 35-37 wherein the copolymer  
14           is dispersed in solvent and acidified.
- 15       40.   The method of any of claims 35-39 wherein the acidified  
16           copolymer has a haze of no more than ten percent as  
17           measured by ASTM method D 1003.
- 18       41.   The method of any of claims 35-40 wherein the alpha-  
19           olefin consists essentially of ethylene.
- 20       42.   The method of any of claims 35-41 wherein metal of said  
21           metal salt is selected from the group consisting of  
22           sodium, lithium, and potassium.
- 23       43.   The method of any of claims 35-42 wherein said ester  
24           comprises methyl acrylate.
- 25       44.   The method of any of claims 35-43 wherein the metal of  
26           said metal salt consists essentially of sodium.

- 69 -

- 1      45. The method of any of claims 35-44 wherein said metal  
2      salt of acrylic or methacrylic acid comprises between  
3      about 1.9 and about 7.5 mole percent of said copolymer.
- 4      46. The method of any of claims 35-45 wherein said esters  
5      of alpha, beta-ethylenically-unsaturated carboxylic  
6      acid comprise between about 2.3 and about 7.4 mole  
7      percent of said copolymer.
- 8      47. The method of any of claims 35-46 wherein said alkali  
9      metal salt of alpha, beta-ethylenically-unsaturated  
10     carboxylic acid comprises between about 3.0 and about  
11     6.5 mole percent of said copolymer.
- 12     48. The method of any of claims 35-47 wherein said esters  
13     of alpha, beta-ethylenically-unsaturated carboxylic  
14     acid comprise between about 2.8 and about 6.3 mole  
15     percent of said copolymer.
- 16     49. The method of any of claims 35-48 wherein the acid is a  
17     polymeric acid.
- 18     50. The method of any of claims 35-48 wherein the acid is  
19     phosphoric acid.

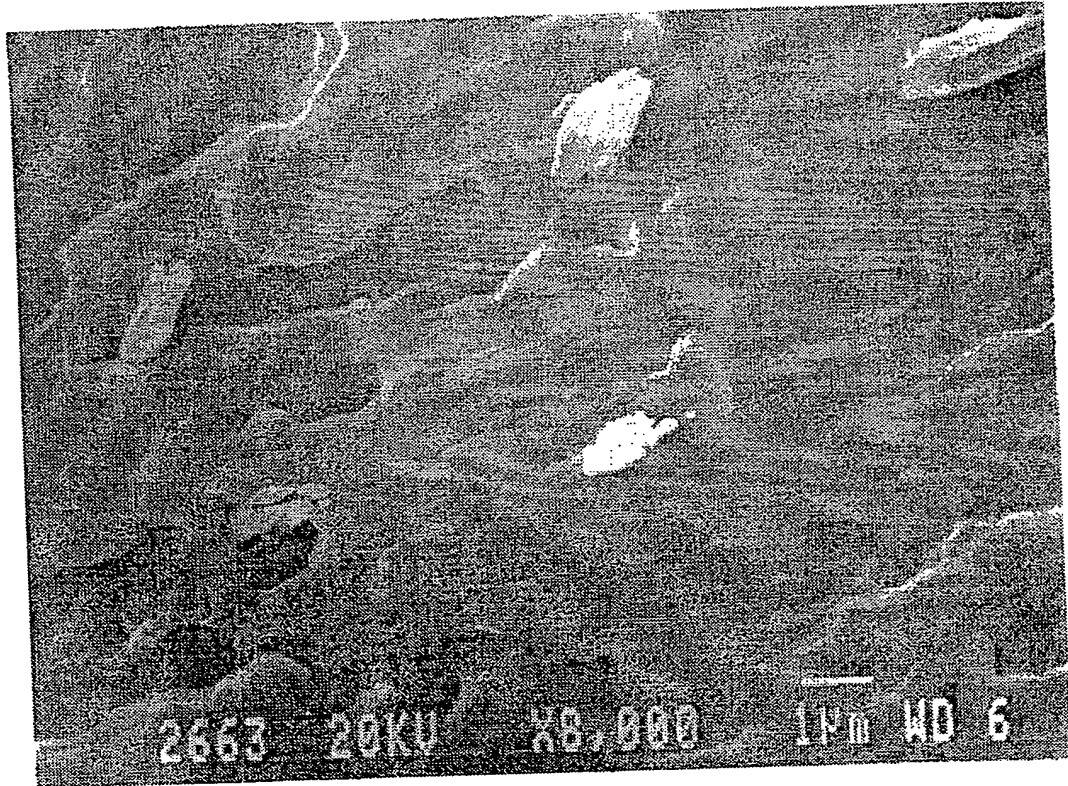


FIGURE 1



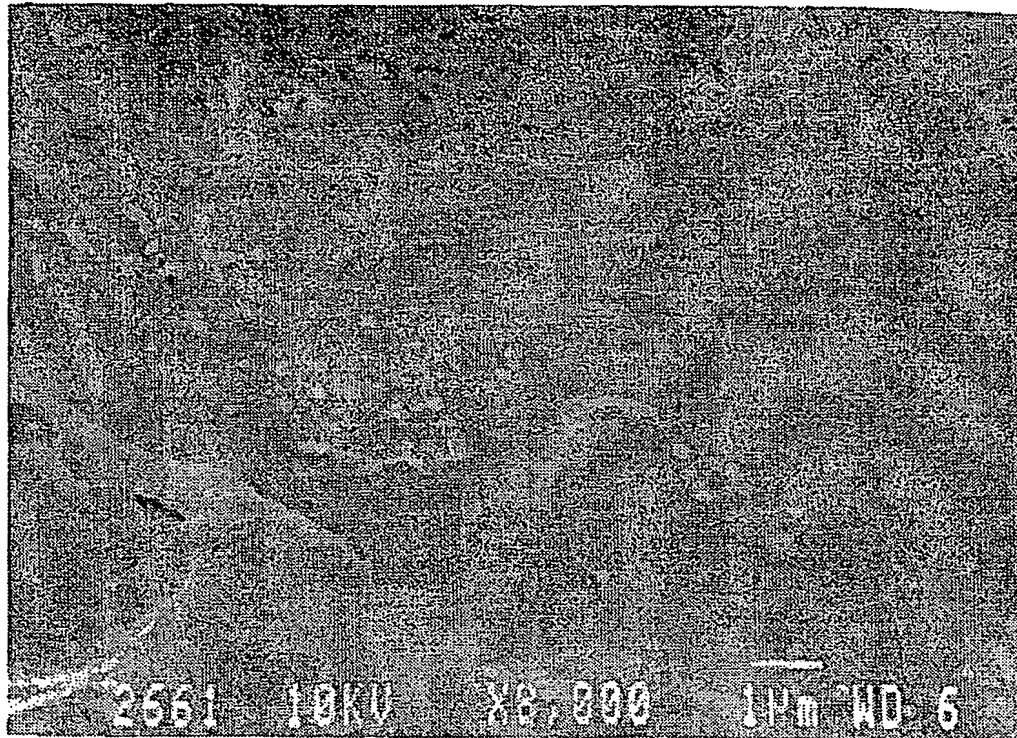


FIGURE 2

# INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US 94/12366**

## A. CLASSIFICATION OF SUBJECT MATTER

C 08 F 8/00, C 08 J 5/18, //(C 08 F 210/02,  
C 08 F 220:06)

According to International Patent Classification (IPC) or to both national classification and IPC **6**

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 08 F, C 08 J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A, 0 194 677 (NIPPON PETROCHEMICALS CO LTD.) 17 September 1986 (17.09.86), claims 1,2,5-7,10; examples. --	1-8, 10, 15-22
A	US, A, 5 218 057 (KURKOV et al.) 08 June 1993 (08.06.93), claims 1-15; examples 1-3; column 5, lines 3-9 (cited in the application). --	1,2, 4-8, 10,11, 15-23, 25
A	GB, A, 1 011 981 (E.I.DU PONT DE NEMOURS AND COMPANY) 01 December 1965 (01.12.65), claims 1,2,8-12,15; page 12, lines 50-54; page 10.	1,2,4, 5,10, 11, 15-18, 27,29

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

### \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search  
**20 February 1995**

Date of mailing of the international search report

**13.03.95**

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

**PUSTERER e.h.**

## INTERNATIONAL SEARCH REPORT

-2-

International application No.  
PCT/US 94/12366

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	product No.24. --	
A	US, A, 3 264 272 (REES) 02 August 1966 (02.08.66), claims 1,3,4,7,8,18,20,30,33 (cited in the application). --	1,4,5, 10, 15-17, 27,29
A	US, A, 3 970 626 (HURST et al.) 20 July 1976 (20.07.76), claims 1,3,4; example 1 (cited in the application). --	1,2, 4,5, 8-11, 15-22, 27,28
A	US, A, 4 638 034 (Mc CLAIN) 20 January 1987 (20.01.87), claims 1-3,5-7 (cited in the application). --	1,2,4, 7,10, 15-23
A	EP, A, 0 115 190 (E.I.DU PONT DE NEMOURS AND COMPANY) 08 August 1984 (08.08.84), page 10, comparative examples 1,3. --	1,3,4, 6-8, 10,15, 16,18
A	US, A, 4 307 211 (ITO et al.) 22 December 1981 (22.12.81), claim 1. -----	1,7,8, 10,15

## ANHANG

zum internationalen Recherchen-  
bericht über die internationale  
Patentanmeldung Nr.

## ANNEX

to the International Search  
Report to the International Patent  
Application No.

## ANNEXE

au rapport de recherche inter-  
national relatif à la demande de brevet  
international n°

PCT/US 94/12366 SAE 100266

In diesem Anhang sind die Mitglieder  
der Patentfamilien der im obenge-  
nannten internationalen Recherchenbericht  
angeführten Patentdokumente angegeben.  
Diese Angaben dienen nur zur Unter-  
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family  
members relating to the patent documents  
cited in the above-mentioned inter-  
national search report. The Office is  
in no way liable for these particulars  
which are given merely for the purpose  
of information.

La présente annexe indique les  
membres de la famille de brevets  
relatifs aux documents de brevets cités  
dans le rapport de recherche inter-  
national visée ci-dessus. Les renseigne-  
ments fournis sont donnés à titre indica-  
tif et n'engagent pas la responsabilité  
de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A2 194677	17-09-86	DE C0 3689007 DE T2 3689007 EP A3 194677 EP B1 194677 JP A2 61209205	21-10-93 05-05-94 05-04-89 15-09-93 17-09-86
US A 5218057	08-06-93	EP A1 548352 EP A4 548352 FI A 930936 FI A0 930936 JP T2 6501519 NO A 930651 NO A0 930651 WO A1 9301219	30-06-93 29-12-93 03-03-93 03-03-93 17-02-94 24-02-93 24-02-93 21-01-93
GB A 1011981		keine - none - rien	
US A 3264272		keine - none - rien	
US A 3970626	20-07-76	BE A 692973 DE A1 1520778 SE B 317194 US A 3876452 NL A 6406361	03-07-67 08-02-73 10-11-69 08-04-75 07-12-64
US A 4638034	20-01-87	keine - none - rien	
EP A2 115190	08-08-84	BR A 8307134 CA A1 1213389 DE C0 3373909 DK A0 6002/83 DK A 6002/83 DK B 167025 DK C 167025 EP A3 115190 EP B1 115190 JP A2 59133217 JP B4 5002687 KR B1 9102467 NO A 834816 NO B 164032 NO C 164032 US A 4690981 US A 4801649 ZA A 8309624	07-08-84 28-10-86 05-11-87 27-12-83 29-06-84 16-08-93 03-01-94 27-12-84 30-09-87 31-07-84 13-01-93 23-04-91 29-06-84 14-05-90 22-08-90 01-09-87 31-01-89 28-08-85
US A 4307211	22-12-81	keine - none - rien	